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GRAHAM'S

ELEMENTS OF CHEMISTRY.

VOL. II.

NEW YORK:

CHARLES E. BAILLIÈRE, 290 BROADWAY.

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ELEMENTS

OF

CHEMISTRY,

INCLUDING THE

APPLICATIONS OF THE SCIENCE IN THE ARTS.

BY

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Second Edition,

REVISED AND ENLARGED.

EDITED BY

HENRY WATTS, B.A., F.C.S.

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ADVERTISEMENT.

The present Volume completes the Work as a Treatise upon Inorganic Chemistry; and it is, accordingly, furnished with an Index of Contents, which applies to both volumes.

From the time which has elapsed since the first publication of these Elements, an amount of alteration and addition had become necessary for properly completing a new edition, which precluded the Author, with his present engagements, from undertaking the task. In these circumstances, he gladly availed himself of the assistance of Mr. Watts, who has supplied a large amount of new matter, including the Supplement, and has edited the volume throughout in the most careful and conscientious manner. The most conspicuous changes now made, by which the work is improved, are the following: —

1. The systematic introduction of the best processes for the separation and quantitative estimation of metals and other important substances, in addition to the description of their properties and reactions. The new methods of *volumetric analysis* are detailed, with the description and applications in particular of Bunsen's General Method.

2. In the Supplement, in which the subjects treated in the first volume are resumed and brought down to the present time: The determination of the most important

Physical constants; viz., the Mechanical Equivalent of Heat; the relations between the Chemical and Magnetic effects of the Electric Current, and the reduction of its force to Absolute Mechanical Measure; also the Measurement of the Chemical Action of Light. The Polarisation of Light is treated in sufficient detail for the wants of the Chemical Student, attention being especially directed to the methods of Optical Saccharimetry, and to the very remarkable relations between Crystalline Form and Molecular Rotatory Power discovered by Pasteur.

3. The modern views of the constitution and classification of Chemical Compounds are explained at considerable length, chiefly according to Gerhardt's Unitary System. This includes the classification of Organic as well as Inorganic Compounds, as indeed every general system of classification must do. In the same portion of the work, the formation and reactions of the principal classes of organic compounds are explained, so far as appeared necessary to the general understanding of their mutual relations.

4. The last portion of the Supplement contains the most recently discovered facts relating to the Non-metallic Elements, and the Metals of the Alkalies and Earths, a prominent place being assigned to the allotropic modifications of certain elements; viz., Boron, Silicon, Sulphur, Selenium, and Phosphorus, and to the methods of obtaining the alkali- and earth-metals in the free state.

THOMAS GRAHAM.

Royal Mint: December, 1857.

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ELEMENTS

OF

CHEMISTRY.

ORDER IV.

METALS PROPER HAVING PROTOXIDES ISOMORPHOUS WITH MAGNESIA.

SECTION I.

MANGANESE.

Eq. 27·67 *or* 345·9; Mn.

THIS element is found in the ashes of plants, in the bones of animals, and in many minerals, of which that employed in the preparation of oxygen is one of the richest. The black oxide of manganese was long known as *magnesia nigra*, from a fancied relation to magnesia alba; but was first thoroughly studied by Scheele, in 1774, and immediately afterwards by Gahn, who obtained from it the metal now called manganese.

From its strong affinity for oxygen, and the very high temperature which it requires for fusion, manganese is one of the most difficult of all the metals proper, to reduce and fuse into a button. Hydrogen and charcoal, at a red heat, reduce the superior oxides of this metal to the state of protoxide, without eliminating the pure metal at that temperature; but

at a white heat, charcoal deprives the metal of the whole of its oxygen. The following process is recommended by M. John for the reduction of manganese: it illustrates the chief points to be attended to in the reduction of the less tractable metals. Instead of a native oxide, an artificial oxide of manganese, obtained by calcining the carbonate in a well-closed vessel, is operated upon. This oxide, which is preferred from being in a high state of division, is mixed with oil and ignited in a covered crucible, so as to convert the oil into charcoal. After several repetitions of this treatment, the carbonaceous mass is reduced to powder, and made into a firm paste by kneading it with a little oil. Finally, this paste is introduced into a crucible lined with charcoal (creuset brasqué), the unoccupied portion of which is filled up with charcoal powder. The crucible is first heated merely to redness for half an hour, to dry the mass and decompose the oil; after which its cover is carefully luted down, and it is exposed for an hour and a half to the most violent heat of a wind-furnace that the crucible itself can support without undergoing fusion. The metal is obtained in the form of a semi-globular mass or button in the lower part of the crucible, but not quite pure, as it contains traces of carbon and silicon derived from the ashes of the charcoal. By igniting the metal a second time in a charcoal crucible, with a portion of borax, John obtained it more fusible and brilliant, and so free from charcoal that it left no black powder when dissolved in an acid.

Manganese is a greyish white metal, having the appearance of hard cast iron. Its density, according to John, is 8·013; while M. Berthier finds it to be 7·05, and Bergmann made it 6·850: according to Hjelm, it is 7·0. From its close resemblance to iron, manganese may be expected to be susceptible of magnetism; but its magnetic powers are doubtful. Péclet has endeavoured to show that manganese can assume and preserve magnetic polarity from the temperature $-4°$ up to 70°, but loses it again at higher temperatures. The small

difference between the atomic weights of iron, manganese, cobalt, and nickel, which are respectively 28, 27·67, 29·52, and 29·57, is remarkable, attended as it is by a great analogy between these metals in many other respects.

Manganese oxidates readily in air, soon falling down as a black powder; in water it occasions a disengagement of hydrogen gas. It is best preserved in naphtha, like potassium, or over mercury. Manganese exhibits five degrees of oxidation, with two intermediate or compound oxides.

OXIDES OF MANGANESE.

Protoxide or manganous oxide .	MnO.
Sesquioxide or manganic oxide .	Mn_2O_3.
Bioxide or Peroxide . . .	MnO_2.
Manganoso-manganic oxide or red oxide	Mn_3O_4, or $MnO + Mn_2O_3$.
Varvicite	Mn_4O_7, or $Mn_2O_3 + 2MnO_2$.
Manganic acid	MnO_3.
Permanganic acid . . .	Mn_2O_7.

Protoxide of manganese; Manganous oxide; MnO, 35·67 *or* 445·9.—This is the oxide existing in the ordinary salts of manganese, which are isomorphous with the salts of magnesia. It may be obtained by fusing at a red heat in a platinum crucible, a mixture of equal parts of pure chloride of manganese and carbonate of soda, with a small quantity of sal-ammoniac. By the reaction between the first-mentioned salts, chloride of sodium is produced, together with the carbonate of manganese, which is decomposed at a red heat, leaving the protoxide of that metal. The hydrogen of the sal-ammoniac at the same time reduces to the state of protoxide any bioxide which may be formed by absorption of oxygen from the air. Any one of the superior oxides of manganese, in the state of fine powder, may be converted into protoxide by

passing hydrogen gas over it, in a porcelain tube at a red heat: the bioxide obtained by igniting the nitrate of the protoxide of manganese was recommended by Dr. Turner as the most easily deoxidated.

Protoxide of manganese is a powder of a greyish green colour, more or less deep. When obtained by means of hydrogen at a low temperature, it absorbs oxygen from the air, soon becoming brown throughout its whole mass, and is, indeed, sometimes a pyrophorus; but when prepared by hydrogen at a high temperature, it acquires more cohesion, and is permanent.

Protoxide of manganese dissolves readily in acids, and is a strong base. Its salts are of a pale rose tint, which is not destroyed by sulphurous or hydrosulphuric acid, and must be considered as a peculiar character of manganous salts. When the solution is colourless, as it sometimes is, the fact is explained, according to M. Görgeu, by the presence of a salt of iron, nickel, or copper; the green or blue tint of the latter metals producing white or a scarcely perceptible violet shade when combined with the rose tint of a salt of manganese. *Caustic alkalies* added to solutions of manganous salts throw down the protoxide of manganese in the form of a white hydrate, which soon absorbs oxygen from the air and becomes brown; when collected on a filter and washed, it ultimately changes into a blackish brown powder, which is the hydrate of the sesquioxide. A similar change is instantaneously produced by the action of chlorine-water upon the white hydrate, or by the addition of chloride of lime to a salt of the protoxide of manganese: but then the hydrated bioxide is formed. Protoxide of manganese resembles magnesia and protoxide of iron, in being but partially precipitated by ammonia. The *alkaline monocarbonates* precipitate white carbonate of manganese, which does not turn brown in the air, and dissolves sparingly in a cold solution of sal-ammoniac. *Bicarbonate of potash* precipitates a strong solution imme-

diately, and renders a dilute solution slightly turbid; but if the solution contains a free acid, so that an excess of carbonic acid is set free, no precipitate is formed. The earthy carbonates do not precipitate manganous salts. *Hydrosulphuric acid* forms no precipitate in neutral solutions of manganous salts containing any of the stronger acids. In a neutral solution of the acetate, a flesh-coloured precipitate is formed after some time; but not if the solution contains free acetic acid. *Sulphide of ammonium* forms in neutral solutions of manganous salts a flesh-coloured precipitate of hydrated sulphide of manganese, insoluble in excess of sulphide of ammonium, but readily soluble in acids. When exposed to the air, it turns brown on the surface, from oxidation. The least trace of iron or cobalt colours it black. *Ferrocyanide of potassium* forms in neutral solutions of manganous salts a white precipitate, having a tinge of red, and soluble in free acids. *Ferricyanide of potassium* forms a reddish precipitate, which is insoluble in acids. Manganous salts, and indeed all compounds of manganese, heated with *borax* or *phosphorus-salt* in the outer blowpipe flame, form an amethyst-coloured bead containing manganoso-manganic oxide, which becomes colourless in the inner flame by reduction of that oxide to the protoxide. This character distinguishes manganese from all other metals. The minutest trace of manganese is discovered by heating the solution with a little *bioxide of lead* and *nitric acid*, when a red tint appears due to the formation of permanganic acid (W. Crum). An equally delicate reaction is obtained in the dry way by heating the substance supposed to contain manganese with *carbonate of soda* on platinum foil in the outer blowpipe flame. The smallest trace of manganese is indicated by the formation of green manganate of soda. The delicacy of the reaction may be increased by adding a little nitre to the carbonate of soda.

Protosulphide of manganese may be procured in the dry way, by heating a mixture of bioxide of manganese and

sulphur. Sulphurous acid is disengaged, and a green powder remains, which dissolves in acids with disengagement of hydrosulphuric acid. The same compound is obtained in the humid way, when acetate of manganese is decomposed by hydrosulphuric acid, or any manganous salt precipitated by an alkaline sulphide. Protosulphate of manganese, decomposed by hydrogen at a red heat, yields an oxisulphide. A crystalline sulphide is obtained by passing the vapour of bisulphide of carbon over hydrated manganic oxide ignited in a porcelain tube: the crystals are iron-black rhombic prisms, having a tinge of green, and yielding a dingy green powder (Völker).

Phosphide of manganese is obtained by exposing an intimate mixture of 10 parts of pure ignited bioxide of manganese, 10 parts of white-burnt bones, 5 parts of white quartz-sand, and 3 parts of ignited lamp-black for an hour in a closed Hessian crucible to a heat sufficient to melt cast-iron,—or by strongly igniting 10 parts of ignited phosphate of manganese, 3 parts of ignited lamp-black, and 2 parts of calcined borax in a crucible lined with charcoal. The product is a very brittle, crystalline regulus of the colour of grey cast-iron, and of specific gravity 5·951. It is permanent in the air, glows when heated in contact with air, and burns with an intense light when heated with nitre. It appears to contain Mn_5P, and is probably a mixture of Mn_3P and Mn_7P, the latter of which compounds is left behind when the substance is treated with hydrochloric acid, while the former dissolves, with evolution of non-spontaneously inflammable phosphuretted hydrogen (Wöhler).

Protochloride of manganese: $MnCl+4HO$; $63{\cdot}17+36$ *or* $789{\cdot}63+450$.—This salt crystallises in thick tables, which are oblong and quadrilateral, and of a rose colour; it is very soluble in water, and slightly deliquescent. The residuary liquid obtained in preparing chlorine by dissolving bioxide of manganese in hydrochloric acid, consists of chloride of manganese contaminated with a portion of sesquichloride of iron.

To remove the latter and obtain a pure chloride of manganese, the solution should be boiled down considerably to expel the excess of acid, diluted afterwards with water, and boiled again with carbonate of manganese, which salt precipitates the whole of the sesquioxide of iron, forming chloride of manganese with its acid (Everitt). If about one fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of soda, a quantity of carbonate of manganese will be obtained sufficient to precipitate the iron from the other three-fourths of the liquid, and applicable to that purpose after it has been washed. The iron may likewise be separated by evaporating the solution of the impure chloride to dryness, heating the residue to low redness in a crucible, as long as hydrochloric acid continues to escape; then leaving it to cool, exhausting with boiling water, and filtering. The hydrated chloride of iron is resolved by the heat into hydrochloric acid and sesquioxide, while the chloride of manganese remains unaltered, and is easily dissolved out by water, all the iron remaining behind. Chloride of manganese, when free from iron, is precipitated white, without any shade of blue, by ferrocyanide of potassium. The crystals retain one of their four equivalents of water at 212° (Brandes), but may be rendered anhydrous at a higher temperature. Brandes finds 100 parts of water to dissolve at 50°, 38·3; at 88°, 46·2; at 144·5°, 55 parts of the anhydrous salt. A higher temperature, instead of increasing the solubility of this salt, diminishes it. From the aqueous solution, chlorine, with the aid of heat, throws down the black hydrated bioxide of manganese. Hypochlorous acid produces a similar result, with evolution of free chlorine. Absolute alcohol dissolves half its weight of the anhydrous chloride of manganese, and affords, by evaporation in vacuo, a crystalline alcoate, containing two equivalents of alcohol.

Chloride of manganese forms two crystalline double salts with chloride of ammonium. One of these, $MnCl.NH_4Cl$,

forms cubical crystals, containing 1 equiv. water, according to Rammelsberg, and 2 eq. according to Hauer. These crystals when ignited leave manganoso-manganic oxide in microscopic pyramids resembling Hausmanite. The other salt, $2MnCl.NH^4Cl+4HO$, forms crystals belonging to the oblique prismatic system (Hautz). Solution of chloride of manganese containing chloride of ammonium, yields, on addition of ammonia and exposure to the air, a precipitate of hydrated manganoso-manganic oxide (Otto).

Protocyanide of manganese is obtained in the form of a yellowish or reddish-white precipitate, on adding cyanide of potassium to the solution of a manganous salt. It quickly turns brown on exposure to the air. It is decomposed by the stronger acids, and dissolves in alkaline cyanides.

The corresponding *fluoride of manganese* forms, with fluoride of silicon, a double salt which is very soluble in water and crystallises in long regular prisms of six sides. The formula of this double salt is, according to Berzelius, $2SiF_3+3MnF+21HO$.

Carbonate of manganese is a white insoluble powder, which acquires a brown tint when exposed in the dry state at 140°. It is decomposed by a red heat. Carbonate of manganese occurs in the mineral kingdom, in the form of *manganese-spar*, but never in a state of purity, being mixed with the carbonates of lime and iron, which have the same crystalline form, viz. the rhombohedral. Its presence in spathic carbonate of iron is said to be the cause why the latter yields an iron peculiarly adapted for the manufacture of steel.

Protosulphate of manganese; Manganous sulphate; MnO,SO_3+7HO.—A solution of this salt, used in dyeing and entirely free from iron, is prepared by igniting bioxide of manganese mixed with about one-tenth of its weight of pounded coal in a gas retort. The protoxide thus formed is dissolved in sulphuric acid, with the addition of a little hydrochloric acid towards the end of the process; the sulphate is evaporated to

dryness, and again heated to redness in the gas retort. The iron is found after ignition in the state of sesquioxide and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition, and remains soluble. The salt may also be obtained by heating bioxide of manganese, previously freed from the carbonates of lime and magnesia by boiling with dilute sulphuric acid, with an equal weight of strong oil of vitriol, and gently igniting the resulting mass for an hour, to decompose the sulphates of iron and copper formed at the same time. The manganous sulphate, which remains unaltered, is then dissolved in water, and the solution evaporated to the crystallising point. The solution is of an amethystine colour, and does not crystallise readily. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it, and rapidly becomes brown in the air; or it is peroxidised at once by passing the cloth through a solution of chloride of lime. The colour thus produced is called manganese-brown.

Crystallised under 42°, the sulphate of manganese gives crystals containing 7HO, which have the same form as sulphate of iron. The crystals which form between 45° and 68°, contain 5HO, and are isomorphous with sulphate of copper. By a higher temperature, from 68° to 86°, a third set of crystals is obtained, which contain 4HO : their form is a right rhombic prism. The sulphate of iron and other sulphates also assume the same form (Mitscherlich). This salt loses 3HO at 243°, but retains 1 eq. even at 400°, like the other magnesian sulphates. M. Kuhn finds, that when a strong solution of the sulphate of manganese is mixed with sulphuric acid and evaporated by heat, a granular salt is precipitated, which contains only one equivalent of water. This sulphate also forms with sulphate of potash a double salt containing 6HO. The anhydrous salt is soluble, according to Brandes, in 2 parts of water at 59°, in 1 part at 122°; but above the latter tempera-

ture, the salt becomes less soluble. The tetra-hydrated salt dissolves in 0·883 part of water at 43·3°; in 0·79 part at 50°; in 0·82 part at 65·8°; in 0·67 part at 99·5°; and in 1·079 part at 2·1°. Manganous sulphate is insoluble in absolute alcohol, but dissolves in 500 parts of spirit of the strength of 55 per cent.

Hyposulphate of manganese; $MnO \,.\, S_2O_5 + 6HO$. For the preparation, see I. 335.—The bioxide of manganese used in preparing it should be previously treated with nitric acid, to dissolve out the hydrated oxide, and be well washed. The salt forms rose-coloured, generally indistinct, crystals, belonging to the doubly oblique prismatic system (Marignac). The *oxalate of manganese* is a highly insoluble salt. The *acetate* is soluble in 3½ parts of cold water, and also in alcohol. Bitartrate of potash dissolves protoxide of manganese, and forms a very soluble double salt, the *tartrate of potash and manganese*, which can be obtained, although with difficulty, in regular crystals.

Sesquioxide of manganese; Manganic oxide; Mn_2O_3; 79·34 *or* 991·8.—This oxide is left of a dark brown, almost black colour, when the nitrate of the protoxide is gently ignited. It also occurs crystallised in the mineral kingdom, although rarely; its density is 4·818, and it is named *braunite* as a mineral species. The hydrate of manganic oxide is formed by the oxidation in air of manganous hydrate. Manganic hydrate also frequently occurs in nature of a black colour, both crystallised and amorphous, and is often mixed with the bioxide of manganese. It constitutes the mineral species *manganite*, of which the density is 4·3 to 4·4, and the formula Mn_2O_3, HO. This hydrate may be artificially prepared by heating finely divided bioxide of manganese with monohydrated sulphuric acid, decomposing the resulting manganic sulphate with water, and washing it thoroughly (Carius). This oxide colours glass of a red or violet tint. The common violet

or purple stained glass contains manganic oxide; also the amethyst.

Manganic oxide is a base isomorphous with alumina and sesquioxide of iron. It dissolves in cold hydrochloric acid without decomposition. Concentrated sulphuric acid combines with it at a temperature a little above 212°, but does not form a solution. Dilute sulphuric acid does not dissolve it, either in the cold or when gently heated, unless manganous oxide is present, even in very small quantities, in which case a violet solution is formed; hence the commonly received statement that manganic oxide forms a red solution with sulphuric acid (Carius). At somewhat elevated temperatures, acids reduce the sesquioxide of manganese to protoxide, with evolution of oxygen.

Manganic sulphate; $Mn_2O_3 . 3 SO_3$.—Prepared by mixing finely divided bioxide of manganese (obtained by passing chlorine gas through a solution of carbonate of soda in which carbonate of manganese is suspended) with monohydrated sulphuric acid to the consistence of a pulp, and gradually heating the mixture in an oil-bath to about 276°, at which point the mass becomes dark green and more mobile. It is then drained on a plate of pumice-stone to remove the greater part of the sulphuric acid; afterwards stirred up in a warm basin with the strongest nitric acid (free from nitrous acid); again drained on pumice-stone; and this treatment repeated several times: lastly, it is dried in the oil-bath at 266°, and preserved in carefully dried tubes.—Manganic sulphate thus obtained is a dark green powder which exhibits no traces of crystallisation. It may be heated to 320° without decomposition, but at higher temperatures gives off oxygen and is reduced to manganous sulphate. At ordinary temperatures it is all but insoluble in concentrated sulphuric and nitric acid; with the former it may be heated nearly to the boiling point without alteration, but, when boiled with the acid, it dissolves as manganous sulphate, with evolution of oxygen.

Heated with concentrated nitric acid to 212°, it turns brown, but resumes its green colour when the acid is evaporated at the lowest possible temperature. In strong hydrochloric acid, it dissolves, like the pure sesquioxide, forming a brown solution, which when heated gives off chlorine till all the sesquioxide of manganese is reduced to protoxide. Organic substances, heated with the dry salt, decompose it with considerable violence. The salt absorbs moisture very rapidly, so that it must always be kept in sealed tubes. Small quantities of it deliquesce in a few seconds, forming a violet solution, which, however, soon becomes brown and turbid from separation of the hydrated oxide. Water decomposes the salt rapidly, especially when heated, separating the pure hydrated sesquioxide. Hence the mode of preparing the hydrate above mentioned. Sulphuric acid, somewhat diluted, decomposes manganic sulphate, converting it into a red-brown powder, which appears to be a basic salt.* Manganic sulphate forms an alum with sulphate of potash (Mitscherlich): this salt occurs native in needle-shaped crystals at Alum Point, on the Great Salt Lake in North America (L. D. Gale).

Sesquichloride of manganese (Mn_2Cl_3) is formed when the sesquioxide is dissolved in hydrochloric acid at a low temperature. The solution is yellowish brown or black, according to its degree of concentration, and is decomposed by a slight elevation of temperature, with evolution of chlorine. A corresponding *sesquifluoride* may be crystallised.

Sesquicyanide of manganese.—A compound of this cyanide is formed, when manganous acetate is mixed with hydrocyanic acid in excess, then neutralised with potash and evaporated. The manganous cyanide then absorbs oxygen, and is converted into hydrated manganic oxide and manganic cyanide, which last combines with cyanide of potassium, and appears, on the cooling of a concentrated solution, in red crystals, which dissolve easily

* Carius, *Ann. Ch. Pharm.* xcviii., 53.

in water (Mitscherlich). This salt is analogous to red prussiate of potash, containing manganese instead of iron, and may, therefore, be represented as containing manganicyanogen—a *manganicyanide of potassium*, $K_3(Mn_2Cy_6)$. As a double cyanide, its formula would be, $3KCy.Mn_2Cy_3$.

Red oxide of manganese, $MnO.Mn_2,O_3$, named by Berzelius manganoso-manganic oxide, is always produced when any oxide of manganese is heated strongly in air. It is a double oxide, being a compound of single equivalents of protoxide and bioxide of manganese. It forms the mineral *Hausmanite*, which differs from manganite in having manganous oxide in place of water. Its density is 4·722. Berthier finds that strong nitric acid dissolves out the protoxide of manganese from the red oxide, and leaves a remarkable hydrate of the bioxide, of which the formula is $4MnO_2 + HO$.

Bioxide or Peroxide of manganese; Black oxide of manganese; MnO_2; 43·67 *or* 545·9.—This is the well-known ore of manganese employed in the preparation of oxygen and chlorine. It generally occurs massive, of an earthy appearance, and contaminated with various substances, such as sesquioxide of iron, silica, and carbonate of lime; but sometimes of a fibrous texture, consisting of small prisms radiating from a common centre. Its density varies from 4·819 to 4·94; as a mineral species it has been named *pyrolusite*.* Another important variety of this ore, known as *wad*, is essentially a hydrate, containing, according to Dr. Turner, 1 eq. of water to 2 eq. of peroxide. A hydrated bioxide, consisting of single equivalents of its constituents, is formed by precipitating the protosalts of manganese with chloride of lime; and the same compound results from the decomposition of the acids of manganese, when diluted with water or an acid. It is possible that the equivalent of this oxide should be doubled, and that its proper

* From πυρ, fire, and λυω, I wash; in allusion to its being employed to discharge the brown and green tints of glass.

formula is Mn_2O_4, corresponding with peroxide of chlorine, ClO_4.

Bioxide of manganese loses one-fourth of its oxygen at a low red heat, and is changed into sesquioxide; at a bright red heat it loses more oxygen, and becomes red oxide, the condition into which all the oxides of manganese pass when ignited strongly in the open air. The bioxide does not unite either with acids or with alkalies. When boiled with sulphuric acid, it yields oxygen gas and a sulphate of the protoxide. In hydrochloric acid it dissolves with gentle digestion, evolving chlorine gas, and forming protochloride of manganese (page 6). It is extensively used in the arts for preparing chlorine, and also to preserve glass colourless by its oxidating action. In the last application, it is added to the vitreous materials in a relatively small proportion, and becomes protoxide, which is not a colouring oxide, while as sesquioxide it would stain glass purple. At the same time it destroys carbonaceous matter, and converts protoxide of iron, which colours glass green, into sesquioxide, which is less injurious.

The mineral *varvicite* was discovered by Mr. R. Phillips among some ores of manganese from Hartshill in Warwickshire. It is distinguished from the bioxide by being much harder, having more of a lamellated structure, and by yielding water freely when heated to redness. Its density is 4·531. It may be supposed to consist of 1 eq. of sesquioxide, and 2 eq. of bioxide with 1 eq. of water (Dr. Turner); its formula is, therefore, $Mn_2O_3 . Mn_2O_4 + HO$.

VALUATION OF BIOXIDE OF MANGANESE.

The numerous applications of the higher oxides of manganese depending upon the oxygen which they can furnish, render it important to have the means of easily and expeditiously estimating their value for such purposes. The value of these oxides is exactly proportional to the quantity of chlorine

which they produce when dissolved in hydrochloric acid, and the chlorine can be estimated by the quantity of protosulphate of iron which it oxidises. Of pure bioxide of manganese 43·7 parts (1 eq.) produce 35·5 parts of chlorine, which oxidise 278 parts (2 eq.) of crystallised protosulphate of iron. Hence 50 grains of bioxide of manganese yield chlorine sufficient to oxidise 317 grains (more exactly, 316·5 grs.) of protosulphate of iron.

50 grains of the powdered oxide of manganese to be examined are weighed out, and also any known quantity, not less than 317 grains, of the sulphate of iron (copperas) employed in chlorimetry. The oxide of manganese is thrown into a flask containing an ounce and a half of strong hydrochloric acid, diluted with half an ounce of water, and a gentle heat applied. The sulphate of iron is gradually added in small quantities to the acid, so as to absorb the chlorine as it is evolved; and the addition of that salt continued, till the liquid, after being heated, gives a blue precipitate with the red prussiate of potash, and has no smell of chlorine, which are indications that the protosulphate of iron is present in excess. By weighing what remains of the sulphate of iron, the quantity added is ascertained; say m grains. If the whole manganese were bioxide, it would require 317 grains of sulphate of iron, and that quantity would, therefore, indicate 100 per cent. of bioxide in the specimen; but if a portion of the manganese only is bioxide, it will consume a proportionally smaller quantity of the sulphate, which quantity will give the proportion of the bioxide, by the proportion: as 317 : 100 :: m : per-centage required. The per-centage of bioxide of manganese is thus obtained by multiplying the number of grains of sulphate of iron oxidised by 0·317. It also follows that the per-centage of chlorine which the same specimen of manganese would afford, is obtained by multiplying the number of grains of sulphate of iron oxidised by 0·2588.

Another mode of estimation is to pass the chlorine gas,

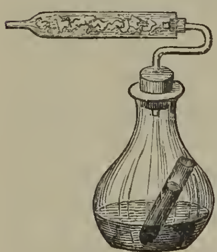
obtained by heating the manganese in a flask with hydrochloric acid, into a solution of sulphurous acid, quite free from sulphuric (it should give no precipitate with chloride of barium); the chlorine converts an equivalent quantity of sulphurous acid into sulphuric. The liquid is then mixed with chloride of barium, and boiled to expel the excess of sulphurous acid, after which the sulphate of baryta is thrown on a filter, washed, dried, ignited, and weighed. The 116·64 gr., or 1 eq. of sulphate of baryta, correspond to 43·7 gr., or 1 eq. of bioxide of manganese.

The value of commercial oxide of manganese may also be estimated by heating it with hydrochloric acid and oxalic acid. The disengaged chlorine then converts the oxalic acid into carbonic acid,—2 eq. of carbonic acid representing 1 eq. of chlorine, and therefore 1 eq. of bioxide of manganese:

$$C_2HO_4 + Cl = 2CO_2 + HCl.$$

A convenient apparatus for the determination is a small light glass flask (fig. 1), of 3 or 4 oz. capacity, having a lipped edge, and fitted with a perforated cork. A piece of tube, about 3 inches long, drawn out at one end, and filled with fragments of chloride of calcium, to absorb water, is fitted by means of a small cork and a bent tube to the mouth of the flask. A short tube closed at one end, and small enough to go into the flask, is used to contain the hydrochloric acid. Fifty grains of the mineral, in the state of very fine powder, are introduced into the flask, together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid in the tube, as shown in the figure: 50 grains of crystallised oxalic acid are then added, the chloride of calcium tube fitted on, and the whole quickly weighed. The flask is then tilted so as to allow the

Fig. 1.



hydrochloric acid to flow out of the tube, and come in contact with the mixture of manganese and oxalic acid, and a gentle heat applied to determine the action. Carbonic acid is then evolved, and escapes through the chloride of calcium tube. To expel the last portions of carbonic acid, the liquid must be ultimately heated till it boils; after which it is left to cool, and weighed: the loss of weight gives the quantity of carbonic acid. Now, as 43·67, the equivalent of bioxide of manganese, is nearly double that of carbonic acid, which is 22, the loss of weight in the apparatus may be taken to represent the quantity of real bioxide in the 50 grains of the sample. [For other methods, see Appendix.]

To obtain a complete appreciation of the value of a sample of manganese, it is not sufficient to know the per-centage of real bioxide in it, — or, which comes to the same thing, the quantity of chlorine it is capable of yielding, — but we must also know the quantity of hydrochloric acid which must be consumed for evolving this chlorine. If the sample consists of pure bioxide, half the acid used will give up its chlorine; if it be pure sesquioxide, only a third of the acid will be changed into chlorine. The quantity of acid required will therefore be greater in the latter case than in the former in the ratio of 3 : 2. Lastly, if the oxide contains lime, baryta, or oxide of iron, these bases will neutralise a portion of the acid without supplying any chlorine. To determine the expenditure of acid, a known weight of the oxide is heated with a known quantity of hydrochloric acid of given strength, the chlorine being suffered to escape, but the hydrochloric acid which would otherwise escape undecomposed being collected in a small receiver moistened on the inside. When the action is over, the acid thus condensed is added to that in the flask, the whole diluted with water, and the quantity of free acid determined by adding a graduated alkaline solution, till the precipitate which forms no longer redissolves on agitation. The quantity of free acid thus determined is then to be de-

ducted from the original quantity, and the difference gives the quantity consumed.

Manganic acid; MnO_3; 51·67 *or* 645·9.—When bioxide of manganese is strongly ignited with hydrate or carbonate of potash in excess, manganic acid is formed, under the influence of the alkali, together with a lower oxide of manganese. Ignition in open vessels, or with an admixture of nitrate of potash, increases the production of the acid, by the absorption of oxygen which then occurs. The product has long been known as *mineral chameleon,* from the property of its solution, which is green at first, to pass rapidly through several shades of colour. But a more convenient process for preparing manganate of potash is that recommended by Dr. Gregory. He mixes intimately 4 parts of bioxide of manganese in fine powder with 3½ parts of chlorate of potash, and adds them to 5 parts of hydrate of potash dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and afterwards ignited in a platinum crucible, but not fused, at a low red heat. The ignited mass, digested in a small quantity of cold water, forms a deep green solution of the alkaline manganate, which may be obtained in crystals of the same colour by evaporating the solution over sulphuric acid in the air-pump. Zwenger, by igniting bioxide of manganese with 3 parts of nitric acid, and evaporating the aqueous solution in vacuo, obtained reddish-brown crystals containing $KO.MnO_3$. On exposure to the air, they became dull and dark green. The manganates were discovered by Mitscherlich to be isomorphous with the sulphates and chromates. It has not yet been found possible to isolate manganic acid. Its salts in solution readily undergo decomposition, unless an excess of alkali is present; and are also destroyed by contact of organic matter, such as paper.

Permanganic acid, Mn_2O_7; 111·34 *or* 1391·8.—When the green solution of manganate of potash, prepared as above directed, is diluted with boiling water, hydrated bioxide of

manganese subsides, and the liquid assumes a beautiful pink or violet colour. The manganic acid is resolved into bioxide of manganese and hypermanganic acid:

$$3MnO_3 = MnO_2 + Mn_2O_7.$$

The permanganate of potash should be rapidly concentrated, without contact of organic matter, and allowed to crystallize. A better process for obtaining this salt is to mix 1 part of bioxide of manganese, in very fine powder, with 1 part of chlorate of potash; introduce this mixture into a solution of $1\frac{1}{4}$ part of caustic potash in the smallest possible quantity of water; evaporate to dryness, during which process a considerable quantity of manganate of potash is formed; then heat the mixture slowly to dull redness; boil the product in water; filter through asbestos, and concentrate by evaporation: the liquid, on cooling, deposits permanganate of potash in crystals. It may be purified by solution in a small quantity of boiling water, and recrystallisation. The crystals are of a dark purple colour, almost black, and soluble in sixteen times their weight of cold water; they were found by Mitscherlich to be isomorphous with perchlorate of potash; they dissolve in 16 parts of water at 60° (Regnault). The permanganates give out oxygen when heated, and are reconverted into manganates. Their solutions have a rich purple colour, and are so stable that they may be boiled, if concentrated. A small portion of a permanganate imparts a purple colour to a very large quantity of water.

When a strong solution of caustic potash is added to a dilute solution of permanganate of potash, the liquid changes colour, assuming first a violet, and afterwards an emerald-green tint. The permanganate is in fact converted into manganate, a double quantity of potash having entered into combination with the acid:

$$KO.Mn_2O_7 + KO = 2(KO.MnO_3) + O.$$

The oxygen thus liberated remains dissolved in the water. This transformation is due to the great basic power of the potash. Acids produce the contrary effect, that is to say, they convert manganates into permanganates.

The insoluble manganate of baryta may be formed by fusing bioxide of manganese with nitrate of baryta; and when mixed with a little water, and decomposed by an equivalent quantity of sulphuric acid, affords free permanganic acid. In Mitscherlich's experiments, the free acid appeared to be a body not more stable than bioxide of hydrogen, being decomposed between 86° and 104°, with escape of oxygen gas and precipitation of hydrated bioxide of manganese. It bleached powerfully, and was rapidly destroyed by all kinds of organic matter. M. Hünefeld, on the other hand, obtained permanganic acid in a state in which it could be preserved, evaporated, redissolved, &c. He washed the manganate of baryta with hot water, by which it is resolved into bioxide of manganese and permanganate of baryta, and then added to it the quantity of phosphoric acid exactly necessary to neutralise the baryta. The liberated permanganic acid was dissolved out, evaporated to dryness, and by a second solution and evaporation, obtained in the form of a reddish-brown mass, crystalline and radiated, which exhibited the lustre of indigo at some points and was entirely soluble in water. When dry permanganic acid was fused in a retort with anhydrous sulphuric acid, and afterwards distilled at a higher temperature, an acicular sublimate of a crimson red colour was obtained, which appeared to be a combination of permanganic and sulphuric acids. (Berzelius's *Traité*, i. 522.) When monohydrated sulphuric acid is poured upon a somewhat considerable quantity of crystallised permanganate of potash, the salt is decomposed with great evolution of heat, red flames bursting out, oxygen being evolved, and manganic oxide set free in dark-brown flakes and shreds like spider-lines. The red flames seem to show that permanganic acid

is gaseous at the high temperature produced by the reaetion. (Wöhler.)

Perchloride of manganese, Mn_2Cl_7, is a greenish yellow gas, which eondenses at 0° F. into a liquid of a greenish-brown colour. This liquid diffuses purple fumes, owing to the formation of hydrochloric and permanganic acids, by the deeomposition of the moisture of the air. It was formed by Dumas by dissolving manganate of potash in oil of vitriol, pouring the solution into a tubulated retort, and adding by dcgrees small portions of chloride of sodium or potassium, completely freed from water by fusion. The perehloride of manganese is the result of a reaction between the liberated hypermanganie and hydrochlorie aeids :

$$Mn_2O_7 + 7HCl = Mn_2Cl_7 + 7HO.$$

A eorresponding *perfluoride of manganese* was formed by Wöhler by distilling, in a platinum retort, a mixture of manganate of potash and fluor-spar in powder, with fuming sulphuric aeid. It is a greenish-yellow gas, whieh likewise produees purple fumes in damp air.

Isomorphous relations of manganese.—There is no other elemcnt whose compounds enter into so many isomorphous groups, and eonnect so large a proportion of the elements by the tie of isomorphism, as manganese. The salts of its prot-oxide are strictly isomorphous with the salts of magnesia and its class; so that manganese belongs to and reprcsents the magnesian family of elements. The same metal connects the sulphur family with the magnesian, by the isomorphism of the sulphates and manganates; and, therefore, sulphur, selenium, and tellurium arc thus allied to the magnesian metals. An equally interesting relation is that of permanganie with perchlorie aeid, and the isomorphism, which it establishes, of 2 equivalents of manganese with 1 equivalent of ehlorine, and the other members of its family.

ESTIMATION OF MANGANESE, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The usual method of precipitating manganese from the solution of a manganous salt, is to add carbonate of soda at a boiling heat. The precipitated carbonate of manganese is then well washed with boiling water, and calcined at a strong red heat, whereby it is converted into manganoso-manganic oxide, Mn_3O_4, containing 72·11 per cent. of manganese. If the solution contains a considerable quantity of ammoniacal salts, it must be evaporated after mixing it with excess of carbonate of soda, and the soluble salts dissolved out of the residue by water.

Manganese is separated from the alkali-metals by means of carbonate of soda or sulphide of ammonium, which latter precipitates it in the form of sulphide. The sulphide is washed with water containing a small quantity of sulphide of ammonium; then redissolved in acid; and the manganese precipitated from the solution by carbonate of soda.

From barium and strontium, manganese is easily separated by means of sulphate of soda, which throws down the baryta and strontia as sulphates; also by sulphide of ammonium. From lime and manganese it is separated by sulphide of ammonium, which, if the solution be sufficiently dilute, precipitates the manganese alone in the form of sulphide. The separation from lime may also be effected by means of oxalate of ammonia, after the addition of chloride of ammonium to keep the manganese in solution.

From alumina and glucina, manganese, if in small or moderate quantity only, may be separated by boiling the solution with potash in an open vessel. The manganese is then precipitated in the form of sesquioxide, while the alumina and glucina are dissolved by the potash. If, however, the proportion of manganese be considerable, this method cannot be used, because the oxide of manganese carries down with it

considerable quantities of alumina and glucina. In this case, the liquid must be mixed with sal-ammoniac and the alumina and glucina precipitated by ammonia. The precipitate, however, always contains small quantities of manganese, which must be separated by subsequent treatment with potash.

SECTION II.

IRON.

Eq. 28 *or* 350; Fe (*ferrum*).

The most remarkable of the metals; the production of which, from the numerous and important applications it possesses, appears to be an indispensable condition of civilisation. Meteoric masses of iron, often so pure as to be malleable, are found widely although thinly scattered over the earth's surface, and probably first attracted the attention of mankind to this metal. Of the occurrence of metallic iron as a terrestrial mineral *in situ*, the best established instances are the species of native iron which accompanies the Uralian platinum, and a thin vein about two inches in thickness, observed in chlorite slate, near Canaan in the United States. In a state of combination, iron is extensively diffused, being found in small quantity in the soil, and in most minerals, and as sulphide, oxide, and carbonate, in quantities which afford an inexhaustible supply of the metal and its preparations, for economical purposes.

Iron differs from all other metals in two points, which greatly affect the methods of reducing it. Its particles agglutinate at a full red heat, although the pure metal is nearly infusible. The oxides of iron, which are easily reduced by combustible matter, thus yield in the furnace a spongy metallic mass, which may admit of being compacted by subsequent

heating and hammering, if the oxide has originally been free from earthy and other foreign matter. Such probably was everywhere the earliest mode of treating the ores of iron, and we find it still followed among rude nations. But iron is also singular in forming, at an elevated temperature, a fusible compound with carbon (cast iron), the production of which facilitates the separation of the metal from every thing extraneous in the ore, and is the basis of the only method of extracting iron extensively practised.

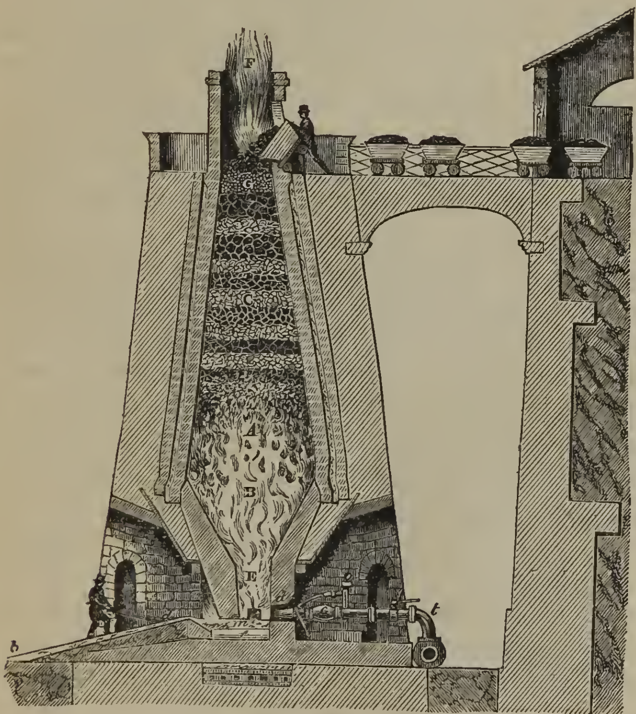
The ore of iron most abundant in the primary formations is the black oxide or *magnetic ore*, which affords the most celebrated and valuable irons of Sweden and the north of Europe, but of which the application is greatly circumscribed from its not being associated with coal. In the secondary and tertiary formations, the anhydrous and hydrated sesquioxide of iron, *red* and *brown hematite*, occur occasionally in considerable quantity, often massive, reniform, and quite pure, at other times pulverulent and mixed with clay. It is employed to some extent in England in the last condition, but only for the purpose of mixing with the more common ore. The crystallised carbonate of iron, or *spathic iron*, is smelted in some parts of the continent, and gives an iron often remarkable for a large proportion of manganese. The celebrated iron of Elba is derived from *specular* or *oligistic iron*, a crystallised sesquioxide. But the consumption of all these ores is inconsiderable, compared with that of the *clay ironstone* of the coal measures. This is the carbonate of the protoxide of iron mixed with variable quantities of clay and carbonates of lime, magnesia, &c.; it is often called the argillaceous carbonate of iron. It is a sedimentary rock wholly without crystallisation, resembling a dark-coloured limestone, but of higher density, from 2·936 to 3·471, and not effervescing so strongly in an acid. It occurs in strata, beds, or bands, as they are also named, from 2 to 10 or 14 inches in thickness, alternating with beds of coal, clay, bituminous

schist, and often limestone. The proportion of iron in this ore varies considerably, but averages about 30 per cent., and after it has been calcined, to expel carbonic acid and water, about 40 per cent.*

SMELTING CLAY IRON-STONE.

The blast furnace, in which the ore is reduced, is of the form represented below, 40 to 65 feet in height, with

Fig. 2.



* Accurate analyses of several Scotch varieties of this ore have been published by Dr. H. Colquhoun (Brewster's *Journal*, vii. 234; or Dr. Thomson's *Outlines of Mineralogy and Geology*, i. 446); and of the French ores, by

an interior diameter of from 14 to 17 feet at the widest part. The cavity of the furnace is entirely filled with fuel and the other materials, which are continuously supplied from an opening near the top; and the combustion maintained by air thrown in at two or more openings, called tuyeres, near the bottom, under a pressure of about 6 inches of mercury, from a blowing apparatus, so as to maintain the whole contents of the furnace in a state of intense ignition. When the air to support the combustion has attained a temperature of 600° or 700°, by passing through heated iron tubes, before it is thrown into the furnace, raw coal may be used as the fuel; but with cold air, the coal must be previously charred to expel its volatile matter, and converted into coke, otherwise the heat produced by its combustion is insufficient. With the ore and fuel, a third substance is added, generally limestone, the object of which is to form a fusible compound with the earthy matter of the ore; it is, therefore, called a *flux*. Two liquid products accumulate at the bottom of the furnace, namely, a glass composed of the flux in combination with the earthy impurities of the ore, which when drawn off forms a solid *slag*, and the carbide of iron, or metal, which is the heavier of the two. It may be drawn from observations made by Dr. Clark, in 1833, on the working of the Scotch blast furnaces, under the *hot blast*, that the relative proportions of the materials, including air, and product of cast iron, are as follows*:—

	Weight.
Coal	5
Roasted iron-stone	5
Limestone	1
Air	11
Average product of cast iron . .	2

M. Berthier, in his *Traité des essais par la voie sèche*, ii. 252, a work which is invaluable for the metallurgic student, and Mitchell's *Practical Assaying*, 8vo.

* Edinburgh Phil. Trans. vol. 13.

The ultimate fixed products are the slag and carburet of iron, but the formation of these is preceded by several interesting changes which the ore successively undergoes in the course of its descent in the furnace. A portion of the oxide of iron is certainly reduced to the metallic state, soon after its introduction, in the upper part of the furnace, by carbonic oxide and volatile combustible matter; but the reduced metal does not then fuse. A large portion of the oxide of iron must combine also, at the same time, with the silica and alumina present in the ore, which act as acids, and a glass be formed, the oxide of iron in which is scarcely reducible by carbon. But this injurious effect of the acid earths is counteracted by the lime of the flux, which, being a more powerful base than oxide of iron, liberates that oxide from the glass when the proportions of the materials introduced into the furnace are properly adjusted, and neutralises the silica; so that the slag eventually becomes a silicate of lime and alumina, with scarcely a trace of oxide of iron. The whole oxide of iron comes thus to be exposed to the reducing action of the volatile combustible, and consequently the whole iron is probably, at one time, in the condition of pure or malleable iron. But when the metal descends somewhat farther in the furnace, it attains the high temperature at which it combines with the carbon of the coke in contact with it, and it fuses for the first time, in the form of carburet of iron. It has not yet, however, attained its ultimate condition. When it reaches, in its descent, the region of the furnace where the heat is most intense, its carbon reacts on the silica, alumina, lime, and other alkaline oxides contained in the fluid slag with which it is accompanied, reducing portions of silicon, aluminum, calcium, and other alkaline metals, which combine with the iron. The proportion of carbon replaced by silicon and metallic bases is generally found to be greater in iron prepared by the hot than by the cold blast, owing, it is presumed, to the higher temperature of the furnace with the hot blast.

The introduction of air already heated to support the combustion of the blast furnace, for which a patent was obtained by Mr. J. B. Neilson, has greatly reduced the proportion of coal required to smelt a given weight of ore, enabling the iron-master, indeed, to effect a saving of more than three-fourths of the coal where it is of a bituminous quality. The air is heated between the blowing apparatus and the furnace, by being made to circulate through a set of arched tubes of moderate diameter, heated by a fire beneath them. The air can be heated in this manner to low redness, or to near 1000°, but there is found to be no proportional advantage in raising its temperature much above the melting point of lead (612°), which is already higher than the point at which charcoal inflames. Considering the great weight of air that enters the furnace, the temperature of that material must greatly affect the whole temperature of the furnace, particularly of the lower part, where the air is admitted, and which part it is desirable should be hottest. Now a certain elevated temperature is required for the proper smelting of the ore, and, unless attained in the furnace, the fuel is consumed to no purpose. The removal of the negative influence of the low temperature of the air, appears to permit the heat to rise to the proper point, which otherwise is attained with difficulty and by a wasteful consumption of fuel. Professor Reich, of Freiberg, has observed that heating the air likewise alters the relative temperatures of different parts of the furnace, depressing in particular, and bringing nearer the tuyeres, the zone of highest temperature. The admixture of steam with the air has, he finds, precisely the opposite effect, elevating the zone of highest temperature in the furnace; so that the effect of the hot blast may be exactly neutralised by mixing steam with the hot air.

Cast iron. — The fused metal is run into channels formed in sand, and thus cast into ingots or pigs, as they are called.

Cast iron is an exceedingly variable mixture of reduced substances, of which the principal is iron combined with carbon. The theoretical constitution to which that variety of it, most definite in its composition, approaches, is the following:—

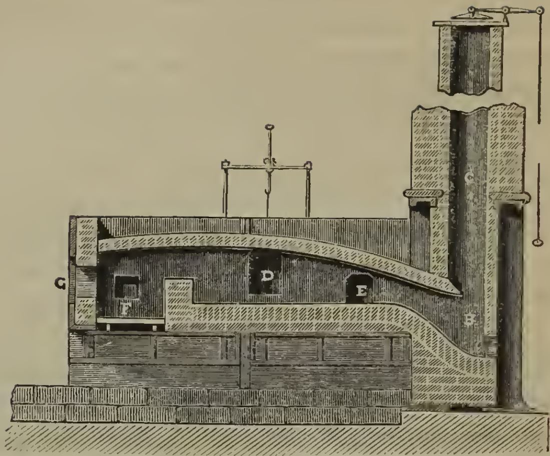
WHITE CAST IRON.

4 equivalents of iron . . .	94·9
1 equivalent of carbon . .	5·1
	100·0

The difference in appearance and quality of the varieties of cast iron is not well accounted for by their composition. The grey or mottled cast iron, forming the qualities Nos. 1 and 2, presents a fracture composed of small crystals, is easily cut by the file, and is preferred for castings. It is generally supposed that a portion of uncombined carbon is diffused through the iron of these qualities, in the form of graphite. No. 3, or white cast iron, is more homogeneous; its fracture exhibits crystalline plates, like that of antimony, and is nearly white; it is exceedingly hard and brittle.

Malleable iron.—The great proportion of cast iron manufactured is afterwards refined, or converted into bar or malleable iron. The mode of effecting this conversion varies with the nature of the fuel. Where coal or coke is used, as in this country, the process consists of two stages. In the first, which is called *refining*, the pig-iron is heated in contact with the fuel in small low furnaces called *refineries*, while air is blown over its surface by means of tuyeres. The effect of this operation is to deprive the iron of a great portion of the carbon and nearly all the silicon associated with it. The metal thus far purified is run out into a trench, and suddenly cooled by pouring cold water upon it. It then forms a greyish-white very brittle mass, blistered on the surface. In

Fig. 3.



this state it is called *fine metal.* It is then ready for the second and principal operation, called the *puddling* process, which consists in heating masses of the iron with a certain access of air in a kind of reverberatory furnace, called the *puddling furnace,* of which Fig. 3. represents a vertical section. This furnace has four doors, two of which, *F* and *G*, serve for the introduction of fuel to the grate; the charge of metal is introduced at *E;* and *D* serves for the insertion of a long poker or spatula, with which the metal is stirred about. The hearth of the furnace has an aperture *B* at the back, for removing the slag. The furnace having been brought to a bright red heat, about four or five hundred-weight of fine metal is introduced, together with one hundred-weight of rich scoriæ or forge cinders (scale-oxide). The metal then fuses, and in this state the workman stirs it about with the poker, so as to expose every part to the flame. The carbon is thus gradually burnt out, partly by the direct action of oxygen in the flame, and partly by cementation with the oxide of iron; and the metal becomes

less fusible, and thick and tenacious, so that it sticks together, and is easily formed into four or five large balls, called blooms. In this condition it is removed by tongs, compressed into a cylindrical form by a few blows of a loaded hammer, and quickly converted into a bar, by pressing it between grooved rollers. The tenacity of the metal is further increased by welding several bars together; a faggot of bars is brought to a white heat in an oblong furnace, and then extended between the grooved rollers into a single bar.

The texture of malleable iron is fibrous. Although the purest commercial form of the metal, it still contains about one-half per cent. of carbon, with traces of silicon and other metals.

Pure iron may, however, be obtained by introducing into a Hessian crucible 4 parts of iron wire cut into small pieces, and 1 part of black oxide of iron; placing above these a mixture of white sand, lime, and carbonate of potash, in the proportions used for glass-making; covering the crucible with a closely fitting lid; and exposing it to a very high temperature. A button of pure metal is thus obtained, the traces of carbon and silicon in the iron having been removed by the oxygen of the oxide. (Mitscherlich.)

Steel.—Only the best qualities of malleable iron, those prepared from a pure ore, and reduced by means of charcoal, such as the Swedish iron, are converted into steel. An iron box is filled with flat bars of such iron and charcoal powder, in alternate layers, and kept at a red heat for forty-eight hours, or longer. The surface of the bars is found afterwards to be blistered, and they have absorbed from 1·3 to 1·75 per cent. of carbon. This is the process of cementation. It is known that iron can be converted into steel without being in actual contact with charcoal, provided the iron and charcoal are in a close vessel together, and oxygen be present, the carbon reaching the surface of the metal in

the form of carbonic oxide gas. The iron becomes harder by this change, and more fusible, but can still be hammered into shape, and cut with a file. The property in which steel differs most from soft iron, is the capacity it has acquired of becoming excessively hard and elastic, when heated to redness and suddenly cooled by plunging it into cold water or oil. This hardness makes steel invaluable for files, knives, and all kinds of cutting instruments. But the steel, when hardened in the manner described, is harder than is required for most of its applications, and also very brittle. Any portion of its original softness can be restored to the steel by heating it up to particular temperatures,—which are judged of by the colour of the film of oxide upon its surface, which passes from pale yellow at about 430°, through straw yellow, brown yellow, and red purple into a deep blue at 580°,—and allowing the steel afterwards to cool slowly. Articles of steel are *tempered* in this manner.

A simple and expeditious method of converting crude or pig-iron into malleable iron and steel, *without the aid of fuel*, has lately been proposed by Mr. H. Bessemer. This process consists in causing cold air to bubble through the liquid iron; under which circumstances the oxygen of the air combines with the carbon of the iron, removing it in the form of carbonic oxide, and generating sufficient heat to keep the iron in the liquid state without external heating, and to sustain the action till the whole, or any required proportion, of the carbon is burnt away. As the quantity of carbon in the metal diminishes, part of the oxygen combines with the iron, converting it into an oxide, which, at the very high temperature then existing in the vessel, melts, and forms a powerful solvent for the earthy bases associated with the iron. At a certain stage of the process, the whole of the crude iron is said to be converted into cast steel of ordinary quality. By continuing the process, the steel thus formed is gradually deprived of its small remaining portion of carbon, and passes

successively from hard to soft steel, steely iron, and ultimately to very soft iron.*

Properties of iron.—Iron is of a bluish-white colour, and admits of a high polish. It is remarkably malleable, particularly at a high temperature, and of great tenacity. Its mean density is 7·7, which is increased by fusion to 7·8439. When kept for a considerable time at a red heat, its particles often form large cubic or octohedral crystals, and the metal becomes brittle. Malleable iron softens before entering into fusion, and in this state it can be *welded*, or two pieces united by hammering them together. The point of fusion of cast iron is 3479°; that of malleable iron is much higher. Cast-iron expands in becoming solid, and therefore takes the impression of a mould with exactness. Iron is attracted by the magnet at all temperatures under an orange-red heat. It is then itself magnetic by induction, but immediately loses its polarity, if pure, when withdrawn from the magnet. If it contains carbon, as steel and cast iron, it is affected less strongly, but more durably, by the proximity of a magnet, becoming then permanently magnetic. Among the native compounds of iron, the black oxide, which forms the loadstone, and the corresponding sulphide, are those which share this property with the metal in the highest degree. A steel magnet loses its polarity at the boiling point of almond oil; a loadstone, just below visible ignition (Faraday).

Iron reduced from the oxide by hydrogen at a heat under redness, forms a spongy mass, which, when exposed to air, takes fire spontaneously at the usual temperature, oxide of iron being reproduced (Magnus). But iron, in mass, appears to undergo no change in dry air, and to be incapable of decomposing pure water at ordinary temperatures. Nor does it

* Chemical Gazette, 1856. p. 336.

appear to be acted upon by oxygen and water together; but the presence of carbonic acid in the water causes the iron to be rapidly oxidated, with evolution of hydrogen gas. In the ordinary rusting of iron, the carbonate of the protoxide appears to be first produced, but that compound gradually passes into the hydrated sesquioxide, and the carbonic acid is evolved. The rust of iron always contains ammonia, probably absorbed from the air; the native oxides of iron also contain ammonia. Iron remains bright in solutions of the alkalies and in lime-water, which appear to protect it from oxidation; but neutral, and more particularly acid salts, have the opposite effect. The corrosion of iron under water appears, in general, to be immediately occasioned by the formation of a subsalt of that metal with excess of oxide, the acid of which is supplied by the saline matter in solution. Articles of iron may be completely defended from the injury occasioned in this way, by contact with the more positive metal zinc, as in galvanized iron (I., 257), while the protecting metal itself wastes away very slowly. Cast iron is converted into a species of graphite by many years' immersion in sea-water, the greater part of the iron being dissolved while the carbon remains.* In open air, iron burns at a high temperature with vivacity, and its surface becomes covered with a fused oxide, which forms smithy ashes. Iron also decomposes steam at a red heat, and the same oxide is formed as by the combustion of the metal in air, namely, the magnetic or black oxide, $FeO.Fe_2O_3$.

Iron dissolves readily in diluted acids, by substitution for hydrogen, which is evolved as gas. Strong nitric acid acts violently upon iron, yielding oxygen to it, and undergoing decomposition. But the relations of iron to that acid when

* Mr. Mallet has collected much information respecting the corrosion of iron, in his First Report to the British Association, on the action of sea and river water upon cast and wrought iron, 1839.

slightly diluted are exceedingly singular; they have been particularly studied by Professor Schönbein.

Passive condition of iron.—Pure malleable iron, such as a piece of clean stocking wire, usually dissolves in nitric acid of sp. gr. 1·3 to 1·35, with effervescence; but it may be thrown into a condition in which it is said by Schönbein to be *passive,* as it is no longer dissolved by that acid, and may be preserved in it for any length of time without change :—1. By oxidating the extremity of the wire slightly, by holding it for a few seconds in the flame of a lamp, and after it is cool dipping it gradually in the nitric acid, introducing the oxidated end first. 2. By dipping the extremity of the wire once or twice in concentrated nitric acid, and washing it with water. 3. By placing a platinum wire first in the acid, and then introducing the iron wire, preserving it in contact with the former, which may afterwards be withdrawn. 4. A fresh iron wire may be introduced in the same manner into the nitric acid, in contact with a wire already passive; this may render passive a third wire, and so on. 5. By making the wire the positive pole or zincoïd of a voltaic battery, introducing it after the negative pole or chloroïd has been placed in the acid. Oxygen gas is then evolved from the surface of the iron wire, without combining with it, as if the wire were of platinum. As the passive state can be communicated by contact of passive iron, so it may be destroyed by contact with active iron (or zinc) undergoing, at the moment, solution in the acid. If passive iron be made a negative pole (chlorous) in nitric acid, it also ceases to resist solution. The indifference to chemical action exhibited by iron when passive, is not confined to nitric acid of the density mentioned, but extends to various saline solutions which are usually acted upon by iron. An indifference to nitric acid of the same kind can also be acquired by other metals as well as iron, particularly by bismuth (Dr. Andrews), but in a much less degree. To account for this remarkable phenomenon various theories have been proposed. Schönbein and Wetzlar attri-

bute it to a peculiar electro-dynamic condition of the surface of the metal, similar to that of the platinum in Grove's gas battery (I. 268—270). Mousson attributes it to a coating of nitrous acid. By others again it has been ascribed to a peculiar antagonism between two forces acting simultaneously on the metal, the one tending to oxidate it at the expense of the nitric acid, the other to cause it to take the place of hydrogen in the nitrate of water, just as when it dissolves in sulphuric acid.* But perhaps the most probable explanation is that which attributes the passive condition of iron to the formation on its surface of a thin film of anhydrous ferric oxide, similar to specular iron. This view is supported by the fact that iron which has been ignited, and is therefore completely covered with black oxide, exhibits the same characters, excepting that, from the greater thickness of the coating, the passive state is more complete. It may also be observed, that iron becomes passive only in liquids which give up oxygen, and that in the voltaic circuit it becomes passive precisely under the circumstances in which it is exposed to oxidation, *i. e.* when it is made the zincoid or positive pole, and that it becomes active again when made the negative pole, that is to say, when the oxide is reduced. The same view is supported by the observation that iron rendered passive in nitric acid immediately begins to dissolve on the addition of hydrochloric acid.

PROTOCOMPOUNDS OF IRON; FERROUS COMPOUNDS.

Protoxide of iron, Ferrous oxide; FeO; 36 *or* 450. — Iron appears to admit of three degrees of oxidation, the protoxide

* Dr. Andrews indeed concludes from observation, that the ordinary chemical action of a hydrated acid upon the metals which dissolve in it, is in general diminished, when the acid is concentrated, by the voltaic association of these metals with such metals as gold, platinum, &c.; while, on the contrary, it is increased when the acid is diluted.—Trans. of the Royal Irish Academy, 1838; or, Becquerel, vol. v. pt. 2, p. 187.

and sesquioxide, which are both basic and correspond respectively with manganous and manganic oxide, and ferric acid. The protoxide is not easily obtained in a dry state, from the avidity with which it absorbs oxygen. The purest anhydrous protoxide is obtained by igniting the oxalate out of contact of air; but even this, according to Liebig, contains a small quantity of metallic iron. The protoxide exists in the sulphate and other salts of iron, formed when the metal dissolves in an acid with evolution of hydrogen.

Solutions of ferrous salts have a green colour. *Potash* or *soda* added to them throws down the protoxide as a white hydrate, which becomes black on boiling, from loss of water. The colour of the white precipitate changes by exposure to air, to grey, then to green, bluish black, and finally to an ochrey red, when it is entirely sesquioxide. *Ammonia* exercises a similar action, but does not precipitate the whole of the oxide, because the precipitate dissolves in the ammoniacal salt produced. *Alkaline carbonates* form a precipitate of carbonate of iron, which is white at first, but soon becomes of a dirty green, and undergoes the same subsequent changes from oxidation. Ferrous salts are not precipitated by *hydrosulphuric acid*, the sulphide of iron being dissolved by strong acids, but give a black sulphide with solutions of *alkaline sulphides*. They give a white precipitate with *ferrocyanide of potassium*, which gradually becomes of a deep blue when exposed to air; with the *ferricyanide*, a precipitate which is at once of an intense blue, being one of the varieties of prussian blue. The infusion of *gall-nuts* does not affect a solution of the protoxide of iron when completely free from sesquioxide.

Protosulphide of iron is prepared by heating to redness, in a covered crucible, a mixture of iron filings and crude sulphur, in the proportion of 7 of the former to 4 of the latter. It dissolves in sulphuric and hydrochloric acids, with evolution of hydrosulphuric acid gas (I. 420.).

A *subsulphide of iron*, Fe_2S, appears to be formed when the sulphate of iron is reduced by hydrogen, one-half of the sulphur coming off in the form of sulphurous acid. This subsulphide is analogous to the subsulphides of copper and lead, which crystallise in octahedrons.

Protochloride of iron crystallises with 4HO, and is very soluble. Like all soluble ferrous salts, it is of a green colour, gives a green solution, and has a great avidity for oxygen.

Protiodide of iron is formed when iodine is digested with water and iron wire, the latter being in excess, and is obtained as a crystalline mass by evaporating to dryness. It was introduced into medical use by Dr. A. T. Thomson. A piece of iron wire is placed in the solution of this salt to preserve it from oxidising. The protiodide of iron dissolves a large quantity of iodine, without becoming periodide, as the excess of iodine may be precipitated by starch.

Protocyanide of iron C_2NFe or FeCy, is as difficult to obtain as the protoxide of iron. When cyanide of potassium is added to a protosalt of iron, a yellowish-red precipitate appears, which dissolves in an excess of the alkaline cyanide, and forms the ferrocyanide of potassium (I., 529.). A grey powder remains on distilling the ferrocyanide of ammonium at a gentle heat; and a white insoluble substance on digesting recently precipitated prussian blue in sulphuretted hydrogen water, contained in a well-stopped phial; these products, although they differ considerably in properties, have both been looked upon as protocyanide of iron. This compound is also obtained as a white deposit on boiling an aqueous solution of hydroferrocyanic acid, H_2FeCy_3. The same solution heated with red oxide of mercury forms cyanide of mercury and white protocyanide of iron. The most remarkable property of this cyanide is its tendency to combine with other cyanides of all classes, and to form double cyanides, or to enter as a constituent into the salt-radicals ferrocyanogen and ferricyanogen, Cy_3Fe and Cy_6Fe_2.

Hydroferrocyanic acid; H_2FeCy_3 or $2HCy,FeCy$. This compound was discovered by Mr. Porrett. It may be obtained by decomposing ferrocyanide of barium with sulphuric acid, or ferrocyanide of potassium with an alcoholic solution of tartaric acid, or ferrocyanide of lead with hydrosulphuric acid. It is soluble in water and alcohol, insoluble in ether, and crystallises by spontaneous evaporation in cubes or four-sided prisms, or sometimes in tetrahedrons. When dry, it may be kept for a long time without alteration in close vessels; but is decomposed on exposure to the air with evolution of hydrocyanic acid, and formation of prussian blue.

Hydroferrocyanic acid unites with most salifiable bases, forming the salts called *ferrocyanides*, whose general formula is M_2FeCy_3, the symbol M denoting a metal. The ferrocyanides of ammonium, potassium, sodium, barium, strontium, calcium, and magnesium, dissolve readily in water; the rest are insoluble or sparingly soluble. Some of them, as the copper and uranium salts, are very highly coloured. Ferrocyanide of potassium has been already described (I. 529.).

Ferrocyanide of potassium and iron; $KFe_2Cy_3 = (KFe), (Cy_3Fe)$.—The bluish-white precipitate which falls on testing a protosalt of iron with the ferrocyanide of potassium or yellow prussiate of potash, *e.g.*, with the protochloride:

$$K_2FeCy_3 + FeCl = KCl + KFe_2Cy_3.$$

It is also obtained in the form of a white crystalline salt (mixed with bisulphate of potash), in the preparation of hydrocyanic acid, by distilling ferrocyanide of potassium with dilute sulphuric acid:

$$2K_2FeCy_3 + 6SO_3 + 6HO = 3(KO,HO,2SO_3) + 3HCy + KFe_2Cy_3.$$

Exposed to the air, it absorbs oxygen and becomes blue. It then affords ferrocyanide of potassium to water, and after all soluble salts are removed, a compound remains, which Liebig names the *basic sesquiferrocyanide of iron*, and represents by the formula $Fe_4.3(Cy_3Fe) + Fe_2O_3$, corresponding,

as will be seen hereafter, with 1 eq. of prussian blue + 1 eq. of sesquioxide of iron. This basic compound is dissolved entirely by continued washing, and affords a beautiful deep blue solution. The addition of any salt causes the separation of this compound. Its solution may be evaporated to dryness without decomposition. The white ferrocyanide of iron and potassium likewise turns blue when treated with chlorine-water or nitric acid, being thereby converted into ferricyanide of iron and potassium (KFe_4Cy_6).

$$2KFe_2Cy_3 + Cl = KFe_4Cy_6 + KCl.$$

This latter compound, which when dry is of a beautiful violet colour, may be regarded as ferricyanide of potassium $K_3Fe_2Cy_6$, in which 2 eq. of potassium are replaced by iron (Williamson).

Ferricyanide of iron, Turnbull's blue; $Fe_3(Cy_6Fe_2)$.—This is the beautiful blue precipitate which falls on adding the ferricyanide of potassium (red prussiate of potash) to a proto-salt of iron. It is formed by the substitution of 3 eq. of iron for the 3 eq. of potassium of the latter salt (I. 530). The same blue precipitate may be obtained by adding to a proto-salt of iron a mixture of yellow prussiate of potash, chloride of soda, and hydrochloric acid. The tint of this blue is lighter and more delicate than that of prussian blue. It is occasionally used by the calico-printer, who mixes it with permuriate of tin, and prints the mixture, which is in a great measure soluble, upon Turkey-red cloth, *raising* the blue colour afterwards by passing the cloth through a solution of chloride of lime containing an excess of lime. The chief object of that operation is indeed different, namely, to discharge the red and produce white patterns, where tartaric acid is printed upon the cloth; but it has also the effect incidentally of precipitating the blue pigment and peroxide of tin together on the cloth, by neutralising the acid of the pre-muriate of tin. This blue is believed to resist the action of

alkalies longer than ordinary prussian blue. It is distinguished from prussian blue by yielding, when treated with caustic potash or carbonate of potash, a solution of ferrocyanide of potassium, and a residue of ferroso-ferric oxide:

$$3Fe_5Cy_6 + 4KO = 2K_2FeCy_3 + Fe_3O_4;$$

whereas prussian blue treated in the same manner yields ferric oxide (Williamson).

Carbonate of iron is obtained on adding carbonate of soda to the protosulphate of iron, as a white or greenish-white precipitate, which may be washed and preserved in a humid condition in a close vessel, but cannot be dried without losing carbonic acid and becoming sesquioxide of iron. It is soluble, like the carbonate of lime, in carbonic acid water, and exists under that form in most natural chalybeates. Carbonate of iron occurs also crystallised in the rhombohedral form of calc-spar, forming the mineral *spathic iron*, which generally contains portions of the carbonates of lime, magnesia, and manganese. It is generally of a cream colour or black, and its density rarely exceeds 3·8. This anhydrous carbonate does not absorb oxygen from the air. Carbonate of iron is also the basis of clay iron-stone. There is no carbonate of the sesquioxide.

Protosulphate of iron, Ferrous sulphate, Green vitriol, Copperas; $FeO.SO_3, HO + 6HO$; 76 + 63 *or* 950 + 787·5.—This salt may be formed by dissolving iron in sulphuric acid diluted with 4 or 5 times its bulk of water, filtering the solution while hot, and setting it aside to crystallise. But the large quantities of sulphate of iron consumed in the arts are prepared simultaneously with alum, by the oxidation of iron pyrites (I. 606).

The commercial salt forms large crystals, derived from an oblique rhomboïdal prism, which effloresce slightly in dry air, and, when at all damp, absorb oxygen and become of a rusty

red colour; hence the origin of the French term *couperose* applied to this salt, and corrupted in our language into copperas. If these crystals be crushed and deprived of all hygrometric moisture by strong pressure between folds of cotton cloth or filter paper, they may afterwards be preserved in a bottle without any change from oxidation. Of the 7HO which sulphate of iron contains, it loses 6HO at 238°, but retains 1 eq. even at 535°. It may, however, be rendered perfectly anhydrous, with proper caution, without any appreciable loss of acid. The anhydrous salt is also obtained in very small crystalline scales by immersing the hydrated crystals in strong boiling sulphuric acid, and leaving the liquid to cool. The salt was observed by Mitscherlich to crystallise at 176°, with 4HO, in a right rhombic prism, like the corresponding sulphate of manganese. When its solution containing an excess of acid is evaporated by heat, a saline crust is deposited, which, according to Kuhn, contains 3HO. The sulphate of iron appears to form neither acid nor basic salts. One part of copperas requires to dissolve it, the following quantities of water, at the particular temperatures indicated above each quantity, according to the observations of Brandes and Firnhaber:—

50°	59°	75·2°	109·4°	114·°	140·0°	183·2°	194°	212°
1·64	1·43	0·87	0·66	0·44	0·38	0·37	0·27	0·30

Ferrous sulphate undergoes decomposition at a red heat, changing into ferric sulphate, and leaves, after all the acid is expelled, the red sesquioxide known as colcothar. This sulphate, like all the magnesian sulphates, forms with sulphate of potash a double salt containing 6HO. A solution of the sulphate of iron absorbs nitric oxide, and becomes quite black; according to Peligot, it takes up the gas in the proportion of 9 parts to 100 anhydrous salt, or one-fourth of an equivalent (I., 342).

Protonitrate of iron, Ferrous nitrate, may be formed by

dissolving the protosulphide in cold dilute nitric acid; the solution evaporated in vacuo yields pale green, very soluble crystals. The solution of the neutral salt is decomposed near the boiling heat, with evolution of nitric acid and copious precipitation of a ferric subnitrate. Iron turnings dissolve in dilute nitric acid and form the same salt, without evolution of gas, the water and acid being decomposed in such a manner as to form ammonia, at the same time that they oxidate the iron.

Protoacetate of iron, Ferrous acetate, is obtained by dissolving the metal or its sulphide in acetic acid. It forms small green prisms which decompose very readily in the air.

Tartrate of potash and iron, Potassio-ferrous tartrate, is prepared by boiling bitartrate of potash with half its weight of iron turnings and a small quantity of water. Hydrogen is evolved, and a white, granular, sparingly soluble salt formed which blackens in the air from absorption of oxygen. It is used medicinally. The iron of this salt is not precipitated by hydrate or carbonate of potash.

SESQUICOMPOUNDS OF IRON; FERRIC COMPOUNDS.

Sesquioxide of iron; Peroxide of iron; Ferric oxide, 80 or 1000.—Occurs very abundantly in nature: 1. as *oligistic* or *specular iron,* in crystals derived from a rhombohedron very near the cube, which are of a brilliant metallic black and highly iridescent. Their powder is red; their density, from 5·01 to 5·22. This oxide forms the celebrated Elba ore.—2. As *red hematite,* in fibrous, mammillated, or kidney-shaped masses, of a dull red colour, very hard, and of sp. gr. from 4·8 to 5·0. This mineral when cut forms the burnishers of blood-stone.—3. also in combination with water, as *brown hematite,* which is much more abundantly diffused than the anhydrous sesquioxide, the granular variety supplying, according to M.

Berthier, more than three-fourths of the iron-furnaces in France. Its density is 3·922; its powder is brown with a shade of yellow, and it dissolves readily in acid, which the anhydrous sesquioxide does not. From analyses by Dr. Thomson and M. Berthier, this mineral appears to unite with 1 eq. of water, as $HO.Fe_2O_3$, analogous to the magnetic oxide of iron, $FeO.Fe_2O_3$. The hydrated sesquioxide produced by the oxidation of iron pyrites, of which it retains the form, contains 1 eq. of water, or 10·31 per cent., and that from the oxidation of the carbonate of iron, 3 eq. of water, or 14·71 per cent., to 2 eq. of sesquioxide (Mitscherlich, *Lehrbuch*, II. 23, 1840). The hydrate is the yellow colouring matter of clay, and with silica and clay it forms the several varieties of ochre.

When metallic iron is oxidated gradually in a large quantity of water, there forms around it a light precipitate of a bright orange yellow colour, which, according to Berzelius, is a ferric hydrate, and of which the empirical formula is $2Fe_2O_3+3HO$, the usual composition of brown hematite. When iron is oxidated in deep water, it is converted, according to E. Davy, into the magnetic oxide, which is possibly formed by cementation from the hydrated sesquioxide. The hydrated sesquioxide is also obtained, by precipitation from ferric salts, by ammonia and by hydrated or carbonated alkali; but never pure, as when an insufficient quantity of alkali is added, a subsalt containing acid is precipitated; and when the alkali is added in excess, a portion of it goes down in combination with the oxide, and cannot be entirely removed by washing. When ammonia is used, the water and excess of the precipitant may be expelled by ignition, and the pure sesquioxide obtained. The latter is not magnetic, and after ignition dissolves with difficulty in acids. When ignited strongly, it loses oxygen and becomes magnetic.

Ferric oxide and its compounds are strictly isomorphous with alumina and the compounds of that earth, and remarkably analogous to them in properties. It is a weak base,

of which the salts have a strong acid reaction, and are decomposed by all the magnesian carbonates, as well as by the magnesian oxides themselves. The solutions of its salts, which are neutral in composition, have generally a yellow tint; but they are all capable, when rather concentrated, of dissolving a great excess of ferric oxide, and then become red. Very dilute solutions of the neutral salts of ferric oxide are decomposed by ebullition, and the oxide entirely precipitated, the acid of the salt then uniting with water as a base (Scheerer).

Iron is most conveniently distinguished by tests, or precipitated for quantitative estimation, when in the state of sesquioxide. The solution of a ferrous salt is usually oxidised by transmitting a current of chlorine through it, or by adding to it, at the boiling point, nitric acid, in small quantities, so long as effervescence is occasioned from the escape of nitric oxide. *Alkalies* and *alkaline carbonates* throw down a red-brown precipitate of hydrated sesquioxide. *Hydrosulphuric acid* converts a sesquisalt of iron into a protosalt, with precipitation of sulphur. *Ferrocyanide of potassium* throws down prussian blue, but the ferricyanide has no effect upon ferric salts beyond slightly changing the colour of the solution. *Sulphocyanide of potassium* produces a deep wine-red solution with ferric salts, which becomes perfectly colourless when considerably diluted with water, provided the iron salt is not in great excess. *Infusion of gall-nuts* produces a bluish-black precipitate — the basis of common writing ink.

A remarkable insoluble modification of the hydrated sesquioxide is produced by boiling the ordinary hydrate (precipitated from the chloride by ammonia) in water for 7 or 8 hours. The colour then changes from ochre-yellow to brick-red, and the hydrate thus altered is scarcely acted upon by strong boiling nitric acid, and but very slowly by hydrochloric acid. In acetic acid, or dilute nitric or hydrochloric acid, it dissolves, forming a red liquid, which is clear by transmitted but turbid

by reflected light; is precipitated by the smallest quantity of an alkali-salt or a sulphate; and on addition of strong nitric or hydrochloric acid, yields a red granular precipitate which re-dissolves on diluting the liquid with water. The modified hydrate does not form prussian blue with ferrocyanide of potassium and acetic acid. It appears to be $Fe_2O_3.HO$, the ordinary precipitated hydrate, after drying in vacuo, being $2Fe_2O_3.3HO$. This insoluble hydrate is likewise precipitated when a solution of the ordinary hydrate in acetic acid is rapidly boiled. The same solution, if kept for some time at 212° in a close vessel, becomes light in colour, no longer forms prussian blue with ferrocyanide of potassium, or exhibits any deepening of colour on addition of a sulphocyanide; strong hydrochloric or nitric acid, or a trace of an alkali-salt, or sulphuric acid, throws down all the ferric oxide in the form of the insoluble hydrate.* It has also been observed that ferric hydrate becomes crystalline and less soluble by long immersion in water, and by exposure to a low temperature.

Black or magnetic oxide of iron, Ferroso-ferric oxide, $FeO.Fe_2O_3$, an important ore of iron, is a compound of the two oxides. It crystallises in regular octohedrons. In this compound, the sesquioxide of iron may be replaced by alumina and by oxide of chromium, and the protoxide of iron by oxide of zinc, magnesia, and protoxide of manganese, without change of form. It was produced artificially, by Liebig and Wöhler, by mixing the dry protochloride of iron with an excess of carbonate of soda, calcining the mixture in a crucible, and treating the mass with water. The double oxide then remains as a black powder, which may be washed and dried without further oxidation. The same chemists, by dissolving the black oxide in hydrochloric acid, and precipitating by ammonia, obtained a hydrate of the double oxide. It was attracted by the magnet, even when in the state of a

* Péan de St. Gilles, *Ann. Ch. Phys.* [3], xlvi. 47.

flocculent precipitate suspended in water. When ignited and anhydrous, this double oxide is much more magnetic than iron itself.

Scale-oxide, $6FeO . Fe_2O_3$. — When iron is heated to redness in contact with air, two layers of scale-oxide are formed, which may be easily separated. The inner layer, which has the composition just given, is blackish grey, porous, brittle, and attracted by the magnet. The outer layer contains a larger proportion of ferric oxide; it is of a reddish iron-black colour, dense, brittle, yields a black powder, and is more strongly attracted by the magnet than the inner layer. The proportion of ferric oxide in the outer layer is between 32 and 37 per cent., and on the very surface as much as 52·8 per cent. (Mosander). The specific gravity of the scale-oxide is 5·48 (Boullay).

Sesquisulphide of iron, or Ferric sulphide, Fe_2S_3, corresponding with the sesquioxide, may be prepared by pouring a solution of a sesquisalt of iron, drop by drop, into a solution of an alkaline sulphide, the latter being preserved in excess. At a low red heat, it loses 2-9ths of its sulphur, and becomes magnetic pyrites. The common yellow iron pyrites is the *bisulphide of iron*. It crystallises in cubes or other forms of the regular system; its density is 4·981. It may be formed artificially by mixing the protosulphide with half its weight of sulphur, and distilling in a retort at a temperature short of redness. The metallic sulphide combines with a quantity of sulphur equal to that which it already possesses, and forms a bulky powder of a deep yellow colour and metallic lustre, upon which sulphuric and hydrochloric acids have no action. This sulphide appears to be of a stable nature, but the lower sulphides of iron oxidate, when moistened, with great avidity. Stromeyer found the native magnetic sulphide of iron to consist of 100 parts of iron combined with 68 of sulphur; and the sulphide left on distilling iron with sulphur at a high temperature, to be of the same composition. It may be

viewed as $5Fe\,S.Fe_2\,S_3$ (Berzelius). It is said to be this compound which is almost always formed when sulphide of iron is prepared in the usual manner.

Sesquichloride of iron, Ferric chloride, $Fe_2\,Cl_3$, is formed when iron is burned in an excess of chlorine. It is volatile at a red heat. Its solution, which is used in medicine, is obtained by dissolving the hydrated sesquioxide of iron in dilute hydrochloric acid. When greatly concentrated, the solution of sesquichloride of iron yields, sometimes orange-yellow crystalline needles, radiating from a centre, which are $Fe_2\,Cl_3 + 12HO$, at other times, large dark yellowish-red crystals, $Fe_2\,Cl_3 + 5HO$. Mixed with sal-ammoniac, and evaporated in vacuo, it affords beautiful ruby-red octohedral crystals, consisting of 2 eq. of chloride of ammonium, and 1 eq. sesquichloride of iron, with 2 eq. of water, $Fe_2\,Cl_3.2NH_4\,Cl + 2HO$. Of this water, the double salt loses 1 eq. at 150°, and the other when dried above 300° (Graham). There is a similar double salt, containing chloride of potassium, but not so easily formed. Sesquichloride of iron is soluble both in alcohol and ether. A strong aqueous solution was found by Mr. R. Phillips to dissolve not less than 4 eq. of freshly precipitated ferric hydrate, becoming deep red and opaque.

Sesqui-iodide of iron is formed in similar circumstances to the preceding sesquichloride.

Sesquicyanide of iron, Ferric cyanide, Fe_2Cy_3, is unknown in the pure state. A solution of it, which is decomposed by evaporation, is obtained by precipitating the potash of the red prussiate by fluoride of silicon. It forms a numerous class of double cyanides. A compound of the two cyanides of iron, like the compound oxide, is obtained as a green powder, when a solution of the yellow prussiate of potash, charged with excess of chlorine, is heated or exposed to air. The precipitate should be boiled with eight or ten times its weight of concen-

trated hydrochloric acid, and well washed. Its formula is, $FeCy.\ Fe_2Cy_3 + 4HO$.*

Hydroferricyanic acid; $H_3Fe_2Cy_6$, *or* $H_3.(Cy_3Fe)_2$, *or* $3HCy.Fe_2Cy_3$, is obtained by decomposing ferricyanide of lead with sulphuric or hydrosulphuric acid. The decanted yellow solution yields, by careful evaporation, brownish needles, which redden litmus strongly, and have a rough sour taste. This solution gives a deep blue precipitate (Turnbull's blue), with ferrous salts. This acid, united with salifiable bases, forms the *ferricyanides* $M_3Fe_2Cy_6$. The potassium salt is described in Vol. I. p. 530.

Prussian blue, $Fe_4 \cdot 3(Cy_3Fe)$, *or* $3FeCy.\ 2Fe_2Cy_3$.—This remarkable substance is precipitated whenever the yellow prussiate of potash is added to a sesquisalt of iron. Thus with the sesquichloride:

$$3K_2FeCy_3 + 2Fe_2Cl_3 = Fe_4.3(Cy_3Fe) + 6KCl_3.$$

Care must be taken to avoid an excess of the yellow prussiate, as the precipitate is apt to carry down a portion of that salt. The precipitate also contains water which cannot be separated from it without decomposition. On the large scale, prussian blue is sometimes prepared by precipitating green vitriol with yellow prussiate of potash, and subjecting the white precipitate, KFe_2Cy_3, to the action of oxidising agents, such as chlorine or nitric acid. This process, however, is likely to yield ferricyanide of iron and potassium, KFe_4Cy_6 (p. 40.), rather than prussian blue, properly so called.

Prussian blue, dried at the temperature of the air, is a light porous body, of a rich velvety blue colour; dried at a higher temperature it is more compact, and exhibits in mass a coppery lustre. It is tasteless, and not poisonous. Alkalies decompose it, precipitating sesquioxide of iron and reproducing an alkaline ferrocyanide. This renders prussian blue of little value in dyeing, as it is injured by washing with soap. Red

* Pelouze, Ann. Ch. Phys. [2], lxix. 40.

oxide of mercury boiled with prussian blue, affords the soluble cyanide of mercury, with an insoluble mixture of oxide and cyanide of iron. Prussian blue is destroyed by fuming nitric acid, but combines with oil of vitriol, forming a white pasty mass, which is decomposed by water.

The combination of prussian blue and sesquioxide of iron, called *basic prussian blue*, was noticed at page 40.

Although there is no *carbonate of the sesquioxide of iron*, the hydrated sesquioxide is dissolved by alkaline bicarbonates, under certain conditions which are not well understood, and a red solution is formed.

Ferric sulphates.—The neutral sulphate, $Fe_2O_3 . 3SO_3$, is formed by adding to a solution of the protosulphate, half as much sulphuric acid as it already contains, and oxidising by nitric acid. It gives a syrupy liquid, without crystallising. This salt is found native in Chili, forming a bed of considerable thickness. It is generally massive, but forms also six-sided prisms, with right summits, which are colourless, and contain 9HO (Rose). Ferric sulphate is soluble in alcohol. It may be rendered anhydrous by a low red heat; but after ignition, it dissolves in water with extreme slowness, like calcined alum.

When hydrated ferric oxide is digested in the neutral sulphate, a red solution is formed, which, according to Maus, is the compound $Fe_2O_3 . 2SO_3$. The rusty precipitate which is formed in a solution of the protosulphate from absorption of oxygen, is another subsulphate, of which the empirical formula is $2Fe_2O_3 . SO_3$. The decomposition may be represented by the following equation:—

$$10(FeO . SO_3) + 5O = 2Fe_2O_3 . SO_3 + 3(Fe_2O_3 . 3SO_3).$$

The neutral ferric sulphate remains in solution.

A *potassio-ferric sulphate*, or *iron alum*, is formed by evaporating a solution of the mixed salts to their point of crystal-

lisation. It is colourless and exactly analogous in composition to ordinary alum (I. 606.). Its formula is $KO \cdot SO_3 + Fe_2O_3 \cdot 3SO_3 + 24HO$.

Another double sulphate is formed, which crystallises in large six-sided tables, and of which the formula is $2(KO \cdot SO^3) + Fe_2O_3 \cdot 2SO_3 + 6HO$ (Maus), when potash is added gradually to a concentrated solution of ferric sulphate, till the precipitate formed ceases to redissolve, and the solution is evaporated in vacuo.

Berzelius designates as *ferroso-ferric sulphate* a combination containing $FeO \cdot SO_3 + Fe_2O_3 \cdot 3SO_3$. It is the salt produced when a solution of the neutral protosulphate of iron is exposed to the air, till no more ochre is precipitated. The solution, which is yellowish red, does not crystallise, but gives the black oxide of iron when precipitated by an alkali. A salt of the same constituents, but in different proportions, forms large stalactites, composed of little transparent crystals, in the copper mine of Fahlun. This last is represented by $3FeO \cdot 2SO_3 + 3(Fe_2O_3 \cdot 2SO_3) + 36HO$ (Berzelius).

Ferric nitrate.—By dissolving iron in nitric acid, without heat, as in Schœnbein's experiments (page 35), a salt is obtained in large, transparent, colourless crystals. From more than one analysis, Pelouze found the constituents of this salt to be in the proportion of $2Fe_2O_3.3NO_5 + 1\frac{1}{2}HO$. Its solution is decomposed by heat, with deposition of ferric oxide. Ordway*, by digesting metallic iron in nitric acid of sp. gr. 1·20, obtained, first a greenish solution, then a red, and ultimately a rusty brown precipitate; and on adding an equal volume of nitric acid of sp. gr. 1·43 as soon as the last precipitate began to form, and cooling the liquid below 60°,—or by evaporating the greenish solution, adding a large excess of nitric acid and cooling,—colourless, oblique, rhombic prisms, were formed containing $Fe_2O_3 \cdot 3NO_5 + 18HO$; they

* Sill. Am. J. [2], ix. 30.

were deliquescent, sparingly soluble in nitric acid, melted at about 116° to a red liquid, and gave off their acid partly at 212°, completely at a red heat. Two ounces of these crystals pounded and mixed with an equal weight of pulverised bicarbonate of ammonia, produced a fall of temperature from +58° to −5°. By adding this compound to recently precipitated ferric hydrate, Ordway obtained basic salts containing from 1 to 8 eq. oxide to 1 eq. acid. The solutions of these salts were of a deep red colour; were not decomposed by boiling or dilution; but when they contained a large excess of oxide, were decomposed by the addition of chloride of sodium and other salts. Hausmann*, by evaporating the solution of iron in nitric acid to a syrup, adding half the volume of strong nitric acid, and leaving the solution to crystallise, obtained colourless prisms containing $Fe_2O_3 . 3NO_5 + 12HO$. By mixing a very concentrated solution of this neutral salt with water till the colour became reddish yellow, then boiling, and adding nitric acid after cooling, an ochre-coloured precipitate was formed, containing $8Fe_2O_3 \cdot 2NO_5 + 3HO$. By adding a very large quantity of water to a highly concentrated and slightly acid solution of the nitrate, an ochre-coloured precipitate was sometimes formed, containing $36Fe_2O_3.NO_5 + 48HO$. By treating iron in excess with nitric acid, a precipitate was obtained having the composition $8Fe_2O_3.NO^5 + 12HO$.

Ferric oxalate is very soluble and does not crystallise. It forms a double salt with oxalate of potash, of a rich green colour, of which the formula is $3(KO.C_2O_3) + Fe_2O_3.3C_2O_3 + 6HO$. The crystals effloresce in dry air. In this double salt, the ferric oxide may be replaced by alumina or oxide of chromium. This salt is formed by dissolving hydrated ferric oxide to saturation in bioxalate of potash (salt of sorrel), and crystallises readily from a concentrated

* Ann. Ch. Pharm. lxxxix. 100.

solution. The circumstance of its being the salt of sesquioxide of iron most easily obtained and preserved in a dry state, should recommend it as a pharmaceutical preparation.

The *benzoate and succinate of ferric oxide* are insoluble precipitates. Hence the benzoate and succinate of ammonia are employed to separate iron from manganese. As both these precipitates are dissolved by acids, the iron solution should be made as neutral as possible. The formula of the succinate is, $Fe_2O_3.\bar{S}$.

Ferric acid, FeO_3.—This compound, which is analogous to manganic acid, is obtained in the form of a potash-salt by exposing metallic iron or ferric oxide to the action of powerful oxidising agents. 1. A mixture of 1 part iron-filings and 2 parts nitre is projected into a capacious crucible kept at a dull red heat, and the crucible removed from the fire as soon as the mixture begins to deflagrate and form a white cloud; if the heat is too strong, the compound decomposes as fast as it is formed. The soft, somewhat friable mass of ferrate of potash thus obtained, may be taken out with an iron spoon, and preserved in well stoppered bottles; or the ferrate of potash may be obtained in solution by treating the fused mass with ice-cold water, leaving the liquid to stand to allow the undissolved ferric oxide to settle down, and then decanting; the solution must not be filtered, as it is immediately decomposed by contact with organic matter. 2. Ferrate of potash is also formed by igniting ferric oxide with hydrate of potash in an open crucible, or with a mixture of hydrate of potash and nitre. 3. Chlorine gas is passed through a very strong solution of caustic potash containing hydrated ferric oxide in suspension, fragments of solid potash being continually added in order to maintain a large excess of alkali in the liquid. The ferrate of potash, being almost insoluble in the strong alkaline liquid, is deposited in the form of a black powder, which may be freed from the greater part of the mother-liquor by drying it on a plate of porous earthenware.

Ferrate of potash is a very unstable compound, and has not been obtained in the crystalline form. Its solution is of a deep red colour, like that of permanganate of potash. The acid has not been obtained in the free state; it appears indeed to be scarcely capable of existing in that state, decomposing, as soon as liberated, into oxygen and ferric oxide. *Ferrate of baryta* is formed by adding a solution of ferrate of potash to a dilute solution of a baryta-salt; it then falls down as a deep carmine-coloured precipitate, which may be washed and dried without changing colour. It gives off oxygen when heated, and is readily decomposed by acids.

Nitroprussic acid; $Fe_2Cy_5(NO_2).H_2$. This acid and its salts were discovered by Dr. Lyon Playfair.* It is formed by the action of nitric acid (or rather of nitric oxide) on hydroferrocyanic acid or a ferrocyanide. The hydroferrocyanic acid is first converted into hydroferricyanic acid:

$$4H_2FeCy_3 + NO_2 = 2H_3Fe_2Cy_6 + 2HO + N;$$

and afterwards, by the further action of the nitric oxide, into nitroprussic acid:

$$H_3Fe_2Cy_6 + NO_2 = Fe_2Cy_5(NO_2).H^2 + HCy.$$

Cyanogen is also evolved and oxamide deposited; but these products are due to a secondary action.

To prepare the potassium or sodium salt, ferrocyanide of potassium (2 eq.) is digested in the cold with ordinary nitric acid (5 eq.) diluted with an equal bulk of water, till it is completely dissolved; the solution boiled till it forms with ferrous salts no longer a dark blue, but a green or slate-coloured precipitate, and then left to crystallise, whereupon it deposits a large quantity of nitre, together with oxamide. The strongly coloured mother-liquor is neutralised with carbonate of potash or soda; boiled; filtered to separate

* Phil. Trans. 1849, ii. 477.

a green or brown precipitate; and again left to crystallise. Nitrate of potash or soda then crystallises out first; and afterwards, by further evaporation, the nitroprussiate. The *sodium-salt* crystallises most readily, forming large ruby-coloured prisms, which dissolve in $2\frac{1}{2}$ parts of water at 60°, and in a smaller quantity of hot water. From the solution of this salt, the silver-salt may be obtained by double decomposition; and this, when decomposed by hydrochloric acid, yields nitroprussic acid. This acid crystallises in dark red, very deliquescent, oblique prisms, which dissolve very readily in water, alcohol, and ether. The aqueous solution is very prone to decomposition.

The general formula of the *nitroprussiates* or *nitroprussides* is $Fe_2Cy_5\,(NO_2).M_2$* : the radical (which might be called *nitro-ferrocyanogen*) may be regarded as 2 eq. of ferrocyanogen, or 1 eq. of ferricyanogen, Fe_2Cy_6, in which 1 eq. of cyanogen is replaced by nitric oxide, NO_2. Most of them are strongly coloured; the ammonium, potassium, sodium, barium, strontium, calcium, and lead salts, dissolve readily in water, forming deep red solutions from which the salts are not precipitated by alcohol. The other nitroprussiates are insoluble, or sparingly soluble. A solution of a nitroprussiate forms, with the solution of an alkaline sulphide, a splendid blue or purple colour, which affords an extremely delicate test of the presence, either of a nitroprussiate, or of an alkaline sulphide.

* This formula was proposed by Gerhardt. Playfair originally gave the formula $Fe_5Cy_{12}(NO)_3.M_5$; and subsequently (*Phil. Mag.* [3.] xxxvi. 360) suggested the simpler formula, $Fe_2Cy_5(NO).M_2$. Gerhardt's formula, however, agrees quite as well with the analyses of the best defined nitroprussiates as either of these, and is more in accordance with certain reactions; viz., that nitroprussiate of sodium, exposed to sunshine, actually gives off nitric oxide; and that when a solution of the barium-salt is treated with red oxide of mercury, part of the nitrogen is converted into nitric acid.

QUANTITATIVE ESTIMATION OF IRON.

Iron is always estimated in the form of sesquioxide. If the solution contains protoxide, either alone or mixed with sesquioxide, it is first boiled with a sufficient quantity of nitric acid to convert the whole of the protoxide into sesquioxide, and then treated with ammonia in excess to precipitate the latter. The precipitate is collected on a filter, washed, dried, and ignited at a moderate red heat; too high a temperature expels a portion of the oxygen. Every 10 parts of pure sesquioxide correspond to 7 parts of metallic iron. In some cases, however, it is necessary to use potash as the precipitant. In that case, the precipitated ferric oxide is very apt to carry down with it a portion of the potash, which is exceedingly difficult to remove by washing. It is best therefore, after having washed it two or three times with hot water, to re-dissolve it in acid and precipitate by ammonia. In other cases, as when the solution contains organic matter, the iron must be precipitated by sulphide of ammonium, because such substances prevent the precipitation of the oxide. The precipitated sulphide, after being washed, is then dissolved in nitric acid, and the iron precipitated by ammonia as before.

Volumetric method.—The quantity of iron in a solution may also be estimated by reducing it all to the state of protoxide, either by sulphurous acid or by metallic zinc (in the former case the excess of sulphurous acid must be expelled by boiling), and then adding, from a graduated burette, a quantity of solution of permanganate of potash, sufficient to convert all the protoxide of iron into sesquioxide:

$$KO \cdot Mn_2O_7 + 10FeO = 2MnO + KO + 5Fe_2O_3.$$

The liquid must contain an excess of acid, to hold the oxide of manganese in solution. The first portions of perman-

ganate added produce no visible effect; but as soon as all the protoxide of iron is converted into sesquioxide, the addition of another drop of the permanganate imparts a rose tint to the liquid. The value of the solution of the permanganate must be previously ascertained by dissolving 1 gramme of iron (harpsichord wire) in hydrochloric acid, and determining the number of divisions of the burette occupied by the quantity of the solution required to convert that quantity of iron into sesquioxide. (Margueritte, *Ann. Ch. Phys.* [3], 18, 244.)

The preceding method may also be applied to determine the quantities of protoxide and sesquioxide of iron in a solution when they occur together,—viz., by first treating a portion of the solution, as it is, in the manner just described; then taking another equal portion, reducing all the iron in it to protoxide by sulphurous acid, and applying the same method to the solution thus reduced. The first determination gives the quantity of iron in the state of protoxide; the second, the total quantity present: the difference is therefore the quantity in the form of sesquioxide.

Separation of iron from the metals previously described.—From the *alkalies* and *alkaline earths*, iron is separated by ammonia, after having been brought to the state of sesquioxide. In the case of the alkaline earths, care must be taken to add but a slight excess of ammonia, to filter quickly, and exclude the air as completely as possible during the filtration; otherwise the free ammonia will absorb carbonic acid from the air, and then throw down the earths in the form of carbonates, together with the ferric oxide. Should such precipitation occur,—which may generally be known by the colour of the oxide,—the precipitate must be re-dissolved and the treatment with ammonia repeated. If the solution contains fixed organic substances, such as sugar, tartaric acid, &c., the iron must be precipitated by sulphide of am-

monium, and the precipitate treated in the manner already described (p. 56.)

From *alumina* and *glucina*, iron is separated by potash, which precipitates the iron, but holds the alumina or glucina in solution. The precipitate, which always contains potash, must then be re-dissolved in acid, and the iron re-precipitated by ammonia.

The separation of iron from *zirconia*, *yttria*, and *thorina*, is effected by adding a sufficient quantity of tartaric acid to prevent the earths from being precipitated when the solution is rendered alkaline, and throwing down the iron by sulphide of ammonium.

From *magnesia* and from *manganous oxide*, iron is most effectually separated by succinate or benzoate of ammonia. The solution, after all the iron has been brought to the state of sesquioxide, is mixed with a sufficient quantity of sal-ammoniac to hold the magnesia or manganous oxide in solution, and very carefully neutralised with ammonia; it is then treated with benzoate or succinate of ammonia, which throws down the iron as ferric benzoate or succinate, leaving the magnesia or manganous oxide in solution. The precipitate is washed and dried, and ignited in an open platinum crucible, so that the air may have sufficient access to it to prevent any reduction of the iron by the carbon of the organic acid. Should such reduction take place, the iron must be re-oxidized by nitric acid. The success of this mode of separation depends entirely on the care with which the acid in the solution is neutralised with ammonia before adding the benzoate or succinate. If too much ammonia has been added, manganese or magnesia goes down with the iron; if too little, a portion of iron remains in solution. The addition of ammonia should be continued till a small quantity of ferric oxide is precipitated, and does not re-dissolve on agitation. The supernatant liquid has then a deep brown colour, the greater part of the iron being still in the solution.

The separation of ferric oxide from manganous oxide may also be effected by agitating the solution with excess of carbonate of lime or baryta, which precipitates the iron but not the manganese. According to J. Schiel *, manganese may be separated from iron by mixing the solution with acetate of soda and passing chlorine through it; bioxide of manganese is then alone precipitated. The methods of separation given at page 7. serve very well for preparing a pure salt of manganese from a solution containing that metal together with iron, but are not adapted for quantitative analysis.

Aridium? This name was given by Ullgren to a metal which he believed to exist in the chrome-iron ores of Röros in Sweden, and in the iron ores of Oernstolso. Its characters very much resemble those of iron. It forms two oxides analogous to those of iron, and presenting, both with liquid reagents and with the blowpipe, characters which might be exhibited by oxides of iron containing a little chromium (vid. *Chem. Gaz.* 1854, 289); Bahr (*Ann. Ch. Pharm.* lxxxvii. 264), endeavoured to prepare the supposed new metal by Ullgren's process, and came to the conclusion that it was merely iron containing a little phosphorus, and perhaps also chromium.

SECTION III.

COBALT.

Eq. 29·52, *or* 369; Co.

Cobalt occurs in the mineral kingdom chiefly in combination with arsenic, as arsenical cobalt, CoAs; or with sulphur and arsenic, as grey cobalt ore, $CoAs.CoS_2$, but contaminated with iron, nickel, and other metals. Its name is that of the Kobolds or evil spirits of mines, and was applied to it by the

* Sill. Am. J. [2], xv. 275.

superstitious miners of the middle ages, who were often deceived by the favourable appearance of its ores. These remained without value, till the middle of the sixteenth century, when they were first applied to colour glass blue. They are now consumed in great quantity for the blue colours of porcelain and stoneware. Cobalt is likewise found in almost all meteoric stones.

To obtain metallic cobalt, the native arsenide is repeatedly roasted, by which the greater part of the arsenic is converted into arsenious acid, and carried off in vapour, while the impure oxide of cobalt, known as *zaffre*, remains. This is dissolved in hydrochloric acid, and the remaining arsenic precipitated as sulphide, by passing a stream of sulphuretted hydrogen through the solution. To get rid of the iron present, the last solution, after filtration, is boiled with a little nitric acid, to peroxidise that metal; and carbonate of potash is added in excess, which throws down carbonate of cobalt and sesquioxide of iron. The precipitate is treated with oxalic acid, which forms an insoluble oxalate of cobalt and soluble ferric oxalate. The oxalate of cobalt is dried and decomposed by ignition in a covered crucible, when the oxide is reduced by the carbon of the acid, which goes off as carbonic acid, while the metallic cobalt remains as a black powder. To separate cobalt from nickel, with which it is almost always associated, the mixed oxalates of cobalt and nickel, obtained by the preceding process, are dissolved in ammonia, after which the liquid is diluted and exposed to the air in a shallow basin for several days. The ammonia evaporates, and the salt of nickel precipitates as a green powder, while the salt of cobalt remains in solution. The liquid is then decanted, and if no additional precipitate subsides from it in twenty-four hours, it is free from nickel, and may be evaporated to dryness. The precipitate of nickel contains a little cobalt.*

Cobalt is a brittle metal, of a reddish grey colour, some-

* For other methods of separating nickel and cobalt, see *Nickel*.

what more fusible than iron, and of the density 8·5131 (Berzelius). Rammelsberg, in five experiments with cobalt reduced by hydrogen, found the specific gravity to vary from 8·132 to 9·495; the mean is 8·957. Pure cobalt is magnetic, but a minute quantity of arsenic causes it to lose that property.

Cobalt is less oxidable in the air or by acids than iron, dissolving slowly in diluted hydrochloric or sulphuric acid, when heated, with evolution of hydrogen; but it is readily oxidised by nitric acid. This metal forms a protoxide and sesquioxide, CoO and Co_2O_3, corresponding with the oxides of iron, and three intermediate oxides, viz., $Co_3O_4 = CoO.Co_2O_3$; $Co_6O_7 = 4CoO.Co_2O_3$; and $Co_8O_9 = 6CoO.Co_2O_3$. According to Fremy, the first of these, viz., Co_3O_4 is a salifiable base combining directly with acetic acid, and existing in several ammonio-salts of cobalt. Fremy has also obtained compound salts of this nature containing a bioxide of cobalt CoO_2

Protoxide of cobalt, Cobaltous oxide, CoO, 37·52 *or* 469.—Prepared by the ignition of the carbonate. This oxide is a powder of an ash-grey colour. It colours glass blue, even when in minute quantity, no other colouring matter having so much intensity. *Smalt blue* is a pounded potash-glass containing cobalt. All compounds of cobalt, when heated with *borax* or *phosphorus-salt*, either in the inner or in the outer blowpipe-flame, impart a splendid blue colour to the bead. This coloration affords an extremely delicate test for cobalt.

The salts of protoxide of cobalt have a reddish colour in solution. *Potash* or *soda* added to these solutions forms a blue precipitate of the hydrated oxide, insoluble in excess of the reagent. *Ammonia* also forms a blue precipitate, which dissolves in excess of ammonia, yielding a red-brown solution. If the cobalt solution contains a large quantity of free acid or of an ammoniacal salt, no precipitate is formed by ammonia. *Alkaline carbonates* precipitate a pink carbonate of cobalt,

soluble in *carbonate of ammonia*. *Hydrosulphuric acid* does not precipitate a solution of cobalt containing either of the stronger acids; but in a solution of acetate of cobalt, or of any cobalt-salt mixed with acetate of ammonia, it forms a black precipitate of protosulphide of cobalt. *Alkaline sulphides* throw down the same precipitate from all solutions of protoxide of cobalt.

Oxide of cobalt appears to combine with alkalies and earths as well as with acids. It dissolves in fused potash, and imparts a blue colour to the compound. Magnesia mixed with a drop of nitrate of cobalt, and then dried and ignited, assumes a feeble but characteristic rose tint. A compound of oxide of cobalt with alumina is obtained by mixing the solution of a salt of cobalt, which must be perfectly free from iron or nickel, with a solution of equally pure alum, precipitating the liquor by an alkaline carbonate, washing the precipitate with care, then drying and igniting it strongly. It forms a beautiful blue pigment, known as cobalt-blue, which may be compared in purity of tint with ultramarine. A compound of oxide of cobalt with oxide of zinc of a fine green colour may be prepared in a similar manner. These coloured compounds often afford useful confirmatory tests of the presence of zinc, alumina, or magnesia. The substance to be examined is placed on platinum foil, moistened with nitrate of cobalt, then dried, and strongly heated in the blowpipe-flame.

Chloride of cobalt, $Co\,Cl$, is obtained by dissolving zaffre or the oxide in hydrochloric acid. Its solution is pink-red, and affords hydrated crystals of the same colour; but when highly concentrated, assumes an intense blue colour, and then affords blue crystals of chloride of cobalt, which are anhydrous (Proust). The red solution is used as a sympathetic ink; characters written with it on paper are colourless and invisible, or nearly so, but when the paper is warmed by holding it near a fire or against a stove, the writing becomes visible and appears of a beautiful blue. After a while, as the salt absorbs

moisture, the colour again disappears, but may be reproduced by the action of heat. If the paper be exposed to too high a temperature, the writing becomes black, and does not afterwards disappear. The addition of a salt of nickel to the sympathetic ink gives a green instead of blue.

The neutral *carbonate of cobalt* is unknown, oxide of cobalt, like magnesia, being thrown down from its solutions by alkaline carbonates, as a carbonate with excess of oxide. The subcarbonate of cobalt is a pale red powder, which contains, according to Setterberger, 2 eq. of carbonic acid, 5 eq. of oxide of cobalt, and 4 eq. of water.

Besides the *sulphate of cobalt* corresponding with green vitriol, another salt was crystallised by Mitscherlich between 68° and 86°, containing 6 eq. of water, $CoO.SO_3 + 6HO$, isomorphous with a corresponding sulphate of magnesia. Sulphate of cobalt forms the usual double salts with the sulphates of potash and ammonia, containing 6HO.

Nitrate of cobalt, $CoO.NO_5$—is obtained by dissolving the metal, the protoxide, or the carbonate in dilute nitric acid. Its solution is carmine-coloured, and on evaporation yields red crystals containing 6 eq. of water; they deliquesce in the air, fuse below 100°, and at a higher temperature give off water and melt into a violet-red liquid, which afterwards becomes green and thick, and is ultimately converted, with violent intumescence and evolution of nitrous fumes, into black sesquioxide of cobalt. Characters written on paper with a solution of this salt assume a peach-blossom colour when heated.

A *sexbasic nitrate*, $6CoO.NO_5 + 5Aq.$, is obtained on adding excess of ammonia to a well boiled solution of the neutral nitrate, carefully protected from the air. It then falls down as a blue precipitate, but on the slightest access of air quickly assumes a grass-green colour and partly redissolves in the liquid.

Cobalt-yellow, $CoO.KO.N_2O_8$.—This compound is formed by adding a solution of nitrite of potash (obtained by passing

the nitrous fumes evolved from a heated mixture of nitric acid and starch into caustic potash) to an acid solution of nitrate of cobalt; nitric oxide and nitrate of potash are then formed, and the cobalt-compound separates in the form of a beautiful yellow crystalline powder:

$$CoO.NO_5 + 2NO_5 + 4(KO.NO_3) = 3(KO.NO_5) + 2NO_2 + N_2O_8.CoO.KO.$$

It is likewise obtained by adding potash, not in excess, to solution of nitrate of cobalt, so as to precipitate a blue basic salt, treating this with a slight excess of nitrite of potash, and adding nitric acid in a thin stream, by means of a pipette. Also by treating nitrate of cobalt with a slight excess of potash, so as to throw down the rose-coloured hydrated oxide, and passing nitric oxide gas into the mixture. This last reaction is so rapid that it may be exhibited as a lecture-experiment. The compound crystallises in microscopic four-sided prisms with pyramidal summits. It is insoluble in cold water, also in alcohol and ether, but when boiled with water gradually dissolves with evolution of acid vapours; the solution yields on evaporation a lemon-yellow salt of different composition. Nitric acid and hydrochloric acid do not act upon it in the cold, but decompose it at a boiling heat, with evolution of nitrous fumes. Hydrosulphuric acid decomposes it very slowly, sulphide of ammonium immediately, forming black sulphide of cobalt. When heated, it assumes an orange-yellow colour, gives off water and afterwards fumes of nitric and hyponitric acids, and leaves sesquioxide of cobalt mixed with nitrite of potash. Its beautiful colour, its permanence, and the facility with which it mixes with other colours, render it well adapted for artistic purposes.*

According to A. Stromeyer†, this salt is a nitrite of co-

* St. Evre, Ann. Ch. Phys. [3], xxxviii. 177.
† Ann. Ch. Pharm. xcvi. 218.

baltic oxide and potash, $Co_2O_3.2NO_3+3(KO.NO_3)$, and its formation may be represented by the equation,

$$2(CoO.SO_3)+5(KO.NO_3)+O=[Co_2O_3.2NO_3+3(KO.NO_3)] \\ +2(KO.SO_3).$$

When a solution of lead is mixed with nitrite of potash and acetic acid, the liquid assumes a yellow colour, but no precipitation takes place; but on adding a cobalt-salt, a yellowish green precipitate (or brownish black and crystalline from dilute solutions) is formed, whose composition is that of the yellow cobalt-compound with half the potash replaced by oxide of lead (Stromeyer).

Phosphate of cobalt, $2CoO.HO.PO_5$, is an insoluble precipitate of a deep violet colour. When 2 parts of this phosphate or 1 part of the arseniate of cobalt are carefully mixed with 16 parts of alumina and strongly ignited for a considerable time, a beautiful blue pigment is obtained, resembling ultramarine; it was discovered by Thénard.

Arseniate of cobalt, $3CoO.AsO_5 + 8HO$, exists as a crystalline mineral called *cobalt-bloom.*

Sesquioxide of cobalt, Cobaltic oxide, Co_2O_3, is formed when chlorine is transmitted through water in which the hydrated protoxide is suspended, or when a salt of theprotoxide is precipitated by a solution of chloride of lime. In the former case, water is decomposed by the chlorine, and hydrochloric acid produced, while the oxygen of the water peroxidises the cobalt;

$$2CoO + HO + Cl = Co_2O_3 + HCl.$$

The sesquioxide of cobalt is precipitated as a black hydrate, containing 2HO. This hydrate, when cautiously heated to 600° or 700°, yields the black anhydrous oxide. When sesquioxide of cobalt is digested in hydrochloric acid, chlorine is evolved, and the protochloride formed. Exposed to a low red heat, the sesquioxide loses oxygen, and the compound oxide, $CoO.Co_2O_3$, is produced. (Hess.) When protoxide of

cobalt is calcined with a borax glass, at a moderate heat, it absorbs oxygen, and a black mass is obtained, which mixed with manganic oxide, serves as a black colour in enamel painting.

Sesquioxide of cobalt acts as a weak base. Phosphoric, sulphuric, nitric, and hydrochloric acids dissolve its hydrate in the cold, without decomposition at first, but the resulting salts are afterwards reduced to salts of the protoxide. A protosalt of cobalt containing a small quantity of a sesquisalt is somewhat deepened in colour. The most permanent of the sesquisalts is the acetate; the hydrated sesquioxide while yet moist dissolves in acetic acid, slowly but completely. The solution, which has an intense brown colour, forms a brown precipitate with alkalies and alkaline carbonates. With ferrocyanide of potassium it forms a dark precipitate, which, if the precipitant is in excess, gives up cyanogen to it, converting it into ferricyanide of potassium and being itself converted into green ferrocyanide of cobalt. Alkaline oxalates colour the solution yellow, forming an oxalate of the oxide Co_3O_4.

According to Fremy, the oxide Co_3O_4 combines also with other acids. The acetate of this oxide is obtained by digesting in dilute acetic acid the hydrated oxide obtained by continued action of oxygen on the blue precipitate thrown down from ordinary cobalt-salts by potash not in excess. Fremy also states that when chlorine is passed into the solution of ordinary acetate of cobalt, a brownish yellow salt is formed containing the base Co_3ClO_3, or Co_3O_4 in which 1 eq. of O is replaced by Cl. This chlorine base exists also in some of the ammonio-compounds of cobalt (pp. 68-72). The oxide Co_3O_4 is obtained in the free state by heating the nitrate or oxalate of cobalt, or the hydrated sesquioxide to redness in contact with the air (Hess, Rammelsberg); but according to Beetz and Winkelblech, the oxide thus obtained is Co_6O_7. When the residue obtained by gently igniting the oxalate in contact with the air is digested in strong boiling hydrochloric acid, the oxide Co_3O_4 remains in hard, brittle, greyish-black micro-

scopic octohedrons having a metallic lustre. The same crystalline compound is obtained by igniting dry protochloride of cobalt, alone or mixed with sal-ammoniac, in dry air or oxygen gas (Schwarzenberg).

A *cobaltic acid*, Co_3O_5, is obtained in combination with potash by strongly igniting the oxide Co_3O_4, or the protoxide, or the carbonate, with pure hydrate of potash. A crystalline salt is then formed which, when dried at 100° C., contains $KO.3Co_3O_5+3HO$, and gives of 1 eq. of water at 130° (Schwarzenberg).

Bioxide of cobalt, CoO_2, has not been obtained in the free state, but exists according to Fremy in the oxycobaltiac salts. (p. 68.)

There exist three *sulphides of cobalt*, a protosulphide, sesquisulphide, and bisulphide.

Sesquicyanide of cobalt has not been obtained in the separate state, but it exists in a class of double cyanides, of which the radical is cobalticyanogen, Cy_6Co_2, analogous to ferricyanogen. The cobalticyanide of potassium, corresponding with the red prussiate of potash, is formed when protoxide of cobalt or its carbonate is dissolved in caustic potash which has been treated with an excess of hydrocyanic acid. It is an anhydrous salt, pale yellow and nearly colourless when pure, and of the same form as the ferricyanide of potassium. Its solution does not affect the salts of iron, but forms a rose-coloured precipitate with those of the protoxide of cobalt.*

A *phosphide of cobalt*, Co_3P, was obtained by Rose, as a grey powder, on passing hydrogen over the subphosphate of cobalt ignited in a porcelain tube. It is also produced by the action of phosphuretted hydrogen on the chloride of cobalt, and may be looked upon as analogous in composition to the former compound, H_3P.

* For further details on the cobalticyanides, *vide* Gmelin's Handbook (translation), vii. 492—497.

Ammoniacal salts of cobalt.—Cobalt-salts treated with excess of ammonia in a vessel from which the air is excluded, unite with the ammonia, forming compounds to which Fremy gives the name of *ammonio-cobalt salts*. Most of them contain 3 eq. ammonia to 1 eq. of the cobalt-salt; thus the chloride contains $CoCl.3NH_3+HO$: the nitrate $CoO.NO_5.3NH_3+2HO$. They are mostly crystallisable and of a rose-colour, soluble without decomposition in ammonia, but decomposed by water with separation of a basic salt. (Fremy.) H. Rose, by treating dry chloride of cobalt with ammoniacal gas, obtained the compound $CoCl.2NH_3$; and similarly an anhydrous sulphate containing $CoO.SO_3.3NH_3$.

When an ammoniacal solution of a cobalt salt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed containing a higher oxide of cobalt (Co_2O_3 or CO_2), and therefore designated generally as *peroxidised ammonio-cobalt salts*. Several of these salts containing different bases are often formed at the same time. Fremy* distinguishes four classes of these compounds, viz., salts of *oxycobaltia, luteocobaltia, fuscocobaltia*, and *roseocobaltia*.

The *oxycobaltia-salts* are formed by the action of the air on concentrated solutions of ammonio-cobalt salts. They have generally an olive colour, are sparingly soluble in the ammoniacal liquid, and are decomposed by water, especially when hot, with evolution of pure oxygen, liberation of ammonia, and separation of a green basic salt containing cobaltoso-cobaltic oxide CO_3O_4. They contain 5 eq. of ammonia associated with 2 eq. of a monobasic salt of bi-oxide of cobalt, CoO_2; thus the nitrate is composed of $2(CoO_2.NO_5).5NH_3$. The nitrate and sulphate crystallise in small prisms containing water of crystallisation (Fremy).

The *luteocobaltia-salts* are formed: 1. By the action of the air on dilute solutions of ammonio-cobalt salts; 2. By the action of a small quantity of water on crystallised oxycobal-

* Ann. Ch. Phys., [3], xxxv. 257.; Chem. Gaz. 1853, 201.

tia-salts; 3. By treating the brown solution, formed by the action of oxygen in excess on ammonio-cobalt salts, with dilute acids; 4. By treating roseocobaltia-salts with excess of ammonia. These salts are of a fine yellow colour, crystallise readily, are tolerably permanent, and resist for some time the action of boiling water. They give no precipitates with alkaline phosphates or carbonates at ordinary temperatures, but are decomposed by boiling potash, with evolution of ammonia and separation of Co_2O_3HO. Dilute acids precipitate them from their aqueous solution in the crystalline state. They contain 1 eq. of a sesquisalt of cobalt, associated with 6 eq. of ammonia; thus, the sulphate = $(Co_2O_3.3SO_3).6NH_3$; the chloride = $Co_2Cl_3.6NH_3$. (Fremy.) This last salt was previously obtained by Rogojski*, who regarded it as the *hydrochlorate of dicobaltinamine* $ClH.N_2H_5co$ [co = $\frac{2}{3}$Co]. He likewise obtained the other salts of the same base by double decomposition.

Fuscocobaltia-salts are formed when an ammoniacal solution of a protosalt of cobalt is exposed to the air, and by the action of water on the oxycobaltia-salts. They are all uncrystallisable, but may be obtained in the solid state by precipitation with alcohol or excess of ammonia. They are slowly decomposed by boiling with water, but quickly on the addition of an alkali, with evolution of ammonia, and precipitation of hydrated sesquioxide of cobalt. They are of a brown colour, and appear to contain basic salts of sesquioxide of cobalt, united with 4 or 5 eq. of ammonia. The nitrate contains $Co_2O_3.2NO_5.4NH_3.3HO$.

Ammonio-chloride of cobalt, after exposure to the air, yields by evaporation in vacuo, an uncrystallisable residue having the characters of the fuscocobaltia-salts, but containing a chlorine-base; its formula is $Co_2Cl_2O.4NH_3.3HO$. By exposing the solution of the ammonio-chloride to the air for

* J. pr. Chem. lvi. 491.

two or three weeks, and then boiling with sal-ammoniac, roseocobaltiacal chloride separates out first, and afterwards a black crystalline compound containing $Co_3ClO_3.NH_3+5HO$.

The *roseocobaltia-salts* are obtained: 1. By slightly acidulating the solution of an ammonio-cobalt salt, which has been exposed to the air; 2. By boiling the solution of an ammonio-cobalt salt, which has been exposed to the air for two or three days, and contains a fuscocobaltia-salt, with a salt of ammonia; 3. By mixing oxycobaltia-salts with boiling solutions of ammoniacal salts. They have a fine red or rose colour, and some of them crystallise readily. Their reactions are similar to those of the luteocobaltia-salts. The nitrate and the neutral sulphate contain 3 eq. of $Co_2O_3.3NO_5$, or $Co_2O_3.3SO_3$, with 5 eq. ammonia. There is also an acid sulphate containing $(Co_2O_3.5SO_3)5NH_3+5HO$, obtained by adding sulphuric acid in excess to an ammoniacal solution of sulphate of cobalt which has stood for some days in contact with the air. Baryta-water added to the solution of the sulphate, throws down roseocobaltiacal oxide, which is rose-coloured, has a strong alkaline reaction, and decomposes on boiling, giving off ammonia and depositing Co_2O_3. The chloride, $Co_2Cl_3.5NH_3.HO$, is obtained by boiling the ammonio-chloride of cobalt, or the chlorine-compound $Co_2Cl_2O.4NH_3$ (p. 69.), or a salt of oxycobaltia, with chloride of ammonium (Fremy).

Genth * and F. Claudet† have also described a compound which appears to be the same as Fremy's hydrochlorate of roseocobaltia, although each assigns to it a different formula. When sulphate or chloride of cobalt is mixed with a large quantity of chloride of ammonium and an excess of ammonia, exposed for some time to the air, and then boiled with excess of hydrochloric acid, a crimson powder gradually separates, oxygen is evolved, and the liquid becomes colourless. This compound dissolves in 244 parts of cold water, and in a smaller

* Ann. Ch. Pharm. lxxx. 275.; Chem. Gaz. 1851, 266.

† Phil. Mag. [4], ii. 253.; Chem. Soc. Qu. J. iv. 355.

quantity of boiling water, but is decomposed by continued boiling, unless hydrochloric acid be added; in that case a solution is obtained, from which the compound crystallises on cooling in ruby-coloured regular octohedrons. Genth assigns to this compound the formula $Co_2O_3.3NH_4Cl$, regarding it as the chloride of a conjugated radical $Co_2O_3.3NH_4$. Claudet finds it to contain 3Cl, 2Co, 5N and 16H, and expresses its composition by one of the following formulæ:—

$$3NH_4Cl + 2NH_2Co; \qquad Cl\left\{\begin{matrix} NH_2Co_2 \\ NH_3NH_4 \\ NHNH_4 \end{matrix}\right\}; \qquad ClN\left\{\begin{matrix} H_2 \\ Co_2 \end{matrix}\right\} + 2ClN\left\{\begin{matrix} H_2 \\ NH_4 \end{matrix}\right\}$$

According to the two latter formulæ, the compound is supposed to contain ammonium in which part of the hydrogen is replaced by NH_4. It might also be regarded as the *hydrochlorate of pentacobaltosamine* $N_5H_{13}Co_2.3HCl$, the base being formed of 5 eq. of ammonia in which 2 eq. of hydrogen are replaced by cobalt. Gregory* assigns to it the formula $Co_2Cl_3 . 5NH_3$, making it identical with Fremy's roseocobaltiacal chloride.

The compound heated in a glass tube gives off ammonia and sal-ammoniac, and leaves CoCl. When the aqueous solution is boiled, ammonia is evolved, and a precipitate formed probably consisting of $Co_3O_4.3HO$, combined with nitride of cobalt. The chlorine compound treated with recently precipitated oxide of silver, yields the oxygen-compound of the same radical; and by double decomposition with various silver salts, the other salts of the base.

The ammonia in all these compounds is in a peculiar state, not exhibiting its usual basic properties, or being recognisable by the usual reagents or replaceable by other bases. Claus attributes this circumstance to the ammonia being in a *passive* state, which is merely another way of expressing the fact, but

* Ann. Ch. Pharm. lxxvii. 125.

affords no explanation. Weltzien supposes the compounds in question to contain compound ammonium-molecules, in which 1 or 2 at. hydrogen are replaced by ammonium itself (an idea first suggested by Mr. Graham), viz., *ammo-cobaltammonium* $N\overbrace{H_2AmCo}$, and *biammo-cobaltammonium* $N\overbrace{HAm_2Co}$ [the symbol Am standing for NH_4]. Thus the *ammonio-cobalt salts,* containing $2NH_3$, may be regarded as neutral salts of ammo-cobaltammonium, and those which contain $3NH_3$ as neutral salts of biammo-cobaltammonium : thus —

$$CoCl.2NH_3 = N\overbrace{H_2AmCo}.Cl; \text{ and}$$
$$CoBr.3NH_3 = N\overbrace{HAm_2Co}.Br.$$

The *fuscocobaltia-salts* may be regarded as basic salts of the sesquioxide of ammo-cobaltammonium, *e. g.*—

$$Co_2O_3.2NO_5.4NH_3 = (N\overbrace{H_2AmCo})_2O_3.2NO_5.$$

The *luteocobaltia*-salts, as neutral salts of the sesquioxide of biammo-cobaltammonium, *e. g.*—

$$Co_2O_3.3NO_5.6NH_3 = (N\overbrace{HAm_2Co})_2O_3.3NO_5\,;$$

The *roseocobaltia*-salts as neutral sesquisalts containing 1 at. of each of the above-mentioned ammoniums, thus—

$$Co_2Cl_3.5NH_3 = \left.\begin{matrix} N\overbrace{H_2AmCo} \\ N\overbrace{HAm_2Co} \end{matrix}\right\}.Cl_3\,;$$

And the *oxycobaltia-salts* as basic salts of the same two ammonium-molecules, *e. g.*—

$$2CoO_2.2SO_3.5NH_3 = \left.\begin{matrix} N\overbrace{H_2AmCo} \\ N\overbrace{HAm_2Co} \end{matrix}\right\}O_4.2SO_3.$$

ESTIMATION OF COBALT, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Cobalt is generally precipitated from its solutions by caustic potash. The precipitate is bluish, and consists of a basic salt, which, however, when heated, is converted into the hydrated protoxide of a dingy rose colour. It must then be washed in hot water, dried and ignited in an atmosphere of hydrogen, by which it is reduced to the metallic state, after which it is weighed. According to Beetz*, the reduction to the metallic state may be dispensed with, an accurate result being obtained by igniting the precipitated oxide till it no longer varies in weight, its composition being then $4Co.Co_2O_3$ or Co_6O_7; but the reduction by hydrogen is perhaps the surer method.

Cobalt is separated from the *alkalies* and *alkaline earths* by sulphide of ammonium, the black sulphide of cobalt being then dissolved in nitro-hydrochloric acid, and the oxide precipitated by potash as above.

From *magnesia* it may also be separated by sulphide of ammonium, sufficient chloride of ammonium being added to hold the magnesia in solution.

From *alumina* and *glucina* it is separated by potash.

The separation of cobalt from *manganese* is difficult. It is best effected by heating the mixed oxides in hydrochloric acid gas, which converts them into chlorides, and then heating the chlorides in a stream of hydrogen, which reduces the cobalt to the metallic state, but leaves the chloride of manganese undecomposed; the latter is then dissolved out by water. Another mode of separation is to digest the mixed oxides in a solution of pentasulphide of calcium, which dissolves the sulphide of cobalt, but leaves the sulphide of manganese undissolved.†

Cobalt is separated from *iron* in the same manner as man-

* Pogg. Ann. lxi. 472.

† Cloez, J. Pharm. [3.] vii. 157.

ganese (p. 58.), viz. by bringing the iron to the state of sesquioxide, then adding chloride of ammonium, neutralising with ammonia, and precipitating the iron by succinate of ammonia.

SECTION IV.

NICKEL.

Eq. 29·57 or 369·6.

This metal resembles iron and cobalt more than any others, and is associated with these metals in meteorites, and in most of the terrestrial minerals which contain it. The principal ore of nickel is arsenical nickel, a mineral having the colour of metallic copper, to which the German miners, having attempted in vain to extract copper from it, gave the name *kupfer-nickel*, or false copper. This mineral was found by Cronstedt of Sweden, in 1751, to contain a particular metal, which he called nickel. Nickel imparts a remarkable whiteness to the metallic alloys which contain it, on which account it has come of late to be valued in the arts, being added to brass to form the well-known imitations of silver.

The metal is prepared from the native arsenide, or from an artificial arsenide called *speiss*, which contains about 54 per cent of nickel, and has been observed by Wöhler to occur in octohedrons with a square base, having the composition Ni_3As. Speiss is a metallic substance which collects at the bottom of the crucibles in which smalt or cobalt-blue is prepared. In that operation, a mixture of quartzy sand, potashes, and the roasted ore of cobalt is fused. The previous roasting never being perfect, a part of the metals escapes oxidation; and hence when the mixture described is fused, the cobalt, which

is more oxidable than nickel and copper, reacts upon the oxides of these metals, and reduces them, while it is itself oxidated: the nickel and copper concentrate in the speiss, while the smalt contains scarcely any of them. A salt of nickel may be obtained by treating speiss in fine powder with an equal weight of sulphuric acid, diluted with four or five times its bulk of water, and gradually adding an equal weight of nitric acid, which occasions the oxidation of both the nickel and the arsenic. The green solution thus obtained, when cooled and allowed to stand for twenty-four hours, deposits much arsenious acid, from which it may be separated by filtration. A quantity of carbonate of potash, equal to half the weight of the speiss, is then added to the solution, which is concentrated and set aside to crystallise. The double sulphate of nickel and potash, $NiO.SO_3 + KO.SO_3 + 6HO$, forms easily, and may be obtained free from arsenic by a second crystallisation. (Dr. Thomson.) The perfect separation of small quantities of cobalt and copper, which these crystals may still contain, requires additional processes.* With the view of obtaining the metal, the insoluble oxalate of nickel may be precipitated from the preceding salt by oxalate of ammonia, washed, dried, and ignited gently in a covered crucible. The oxalic acid reduces the oxide of nickel, and the metal remains in a spongy state. It is pyrophoric, like manganese and iron prepared in the same manner, if the temperature of reduction has been low. To obtain the metal in a solid mass, it should be fused in a crucible covered with pounded glass. The oxide of nickel is very easily reduced both by carbonic oxide and by hydrogen.

Nickel, when free from cobalt, is silver-white, unalterable in air, and highly ductile. Its density, according to Richter, is 8·279, and after being forged 8·666. Nickel is magnetic nearly to the same extent as iron. Magnets composed of this metal lose their polarity at 630° (Faraday). It is somewhat more fusible than iron. Nickel forms two oxides correspond-

* Berzelius, Traité, tom. i. p. 486.; see also pp. 78—80. of this volume.

ing with the protoxide and sesquioxide of iron; but the double compound of the two oxides of nickel, corresponding with the black oxide of iron, has not been observed.

Protoxide of nickel, NiO, 37·57, or 469·6, may be obtained by the ignition of the carbonate or nitrate of nickel, or by precipitation from its salts by an alkali, as a dark ash-coloured powder, or as a bulky hydrate of an apple-green colour, NiO HO. Oxide of nickel is very soluble in acids, but not in potash or soda. Ammonia dissolves it, and forms an azure-blue solution, from which oxide of nickel is precipitated by potash, baryta, and strontia, having a considerable tendency to combine with salifiable bases. The solutions of its salts have all a green colour, much more intense than that of the ferrous salts. They are not precipitated by hydrosulphuric acid when a strong acid is present, but afford a black sulphide with alkaline sulphides. Carbonate of nickel is of a pale green-colour and soluble in carbonate of ammonia.

Peroxide or *sesquioxide of nickel,* Ni_2O_3, is obtained as a black powder, by exposing the hydrated protoxide suspended in water to a stream of chlorine gas. It does not combine with acids, and in other respects resembles sesquioxide of cobalt.

Besides a *protosulphide,* NiS, a *subsulphide of nickel,* Ni_2S, is formed, like that of manganese, by decomposing the ignited sulphate of nickel with hydrogen. A *bisulphide of nickel* also exists in combination as a constituent of the mineral nickel-glance, NiS_2.NiAs.

Chloride of nickel NiCl, forms a solution of an emerald-green colour, and yields by evaporation a hydrated salt of the same colour, which becomes yellow when deprived of its water of crystallisation. Chloride of nickel, sublimed at a high temperature without access of air, forms golden scales which dissolve with difficulty.

Sulphate of nickel crystallises from a strong solution in slender green prisms, isomorphous with Epsom salt, of which the composition is $NiO.SO_3 + 7HO$. At a higher temperature, it

crystallises with 6 eq. of water $NiO.SO_3 + 6HO$, like the magnesia and cobalt salts, and in the same form. Mitscherlich made the singular observation, that when the crystals containing 7 eq. of water are exposed, in a close glass vessel, to a day of sunshine, or kept for some time in a temperate place, they change their form, becoming a mass of small crystals, of which the form is the regular octohedron. The original crystals become opaque from this change, but lose none of their combined water. Sulphate of nickel forms the usual double salts with the sulphates of potash and ammonia.

Nickel also forms ammonio-compounds analogous to the ammonio-cobalt salts; *e. g. the ammonio-chloride* = $3NH_3.NiCl = \overbrace{NHAm_2Ni}.Cl$; *ammonio-sulphate* = $3NH_3.NiSO_4 = \overbrace{NHAm_2Ni}.SO_4$, &c.

The useful white *alloy of nickel*, German silver or *packfong*, is formed by fusing together 100 parts of copper, 60 of zinc, and 40 of nickel.

ESTIMATION OF NICKEL, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Nickel is best precipitated from its solutions by caustic potash which throws down an apple-green precipitate of the hydrated protoxide, and if the liquid be heated, leaves not a trace of nickel in the solution. The precipitate must be washed with hot water, dried, ignited, and weighed; it then consists of pure protoxide of nickel, containing 78·57 per cent of the metal.

In separating nickel from other metals, it is often necessary to precipitate it by sulphide of ammonium; this precipitation is attended with difficulties, because the sulphide of nickel is somewhat soluble in the alkaline sulphide. To make the precipitation as complete as possible, Rose directs that the solution be diluted with a considerable quantity of water, and then treated with sulphide of ammonium, as nearly colourless as it can be obtained, avoiding a large excess of the precipitant and

likewise an excess of ammonia; the glass is then to be covered up with filtering paper, and left in a warm place. Under these circumstances, the excess of sulphide of ammonium is decomposed by the oxygen and carbonic acid of the air, without risk of the sulphide of nickel being oxidised. As soon as the supernatant liquid has lost its brown colour, the precipitate is collected on a filter and washed, as quickly as possible, with water containing a little sulphide of ammonium. It must then be dissolved in nitro-hydrochloric acid, and the nickel precipitated by potash as above.

The methods of separating nickel from all the preceding metals except cobalt, are the same as those given for cobalt (p. 73.).

The separation of nickel from cobalt itself is difficult. The best method is perhaps that given by H. Rose*, depending on the fact that protoxide of cobalt in solution is converted by chlorine into sesquioxide, whereas with nickel this change does not take place. The metals or their oxides being dissolved in excess of hydrochloric acid, the solution is diluted with a large quantity of water, about a pound of water to a gramme of the metals or their oxides. Chlorine gas is then passed through the solution for several hours, till in fact the space above the liquid becomes permanently filled with the gas; carbonate of baryta is then added in excess, the whole left to stand for 12 or 18 hours, and shaken up from time to time. The precipitate, consisting of sesquioxide of cobalt and carbonate of baryta, is then collected on a filter, and washed with cold water. The filtered liquid, which has a pure green colour, contains all the nickel without a trace of cobalt. The precipitate is boiled with hydrochloric acid to convert the sesquioxide of cobalt into protoxide, and dissolve it together with the baryta; the latter is then precipitated by sulphuric acid, and the cobalt from the filtrate by potash. The nickel is also precipitated by potash after the removal of any baryta that the solution may contain

* Handbuch der Analytischen Chemie (Berlin, 1851), ii. 164.

by sulphuric acid. This method, if properly executed, gives very exact results. The chief precautions to be attended to, are to add a large excess of chlorine, and not to filter too soon, because the precipitation of sesquioxide of cobalt by carbonate of baryta takes a long time.

Liebig has given several methods of separating these two metals, founded on the difference of their reactions with cyanide of potassium. 1. The oxides of the two metals are treated with hydrocyanic acid and then with potash, and the liquid warmed till the whole is dissolved (pure cyanide of potassium, free from cyanate may also be used as the solvent). The reddish-yellow solution is boiled to expel free hydrocyanic acid, whereupon the cobaltocyanide of potassium (K_2CoCy_3), formed in the cold, is converted into cobalticyanide ($K_3Co_2Cy_6$), while the nickel remains in the form of cyanide of nickel and potassium ($KNiCy_2$). Pure and finely-divided red oxide of mercury is then added to the solution while yet warm, whereby the whole of the nickel is precipitated partly as oxide, partly as cyanide, the mercury taking its place in the solution. The precipitate contains all the nickel, together with excess of mercuric oxide; after washing and ignition, it yields pure oxide of nickel. The filtered solution contains all the cobalt in the form of cobalticyanide of potassium. It is supersaturated with acetic acid, boiled with sulphate of copper, which precipitates the cobalt in the form of cobalticyanide of copper ($Cu_3Co_2Cy_6.7HO$), and the precipitate retained in the liquid at a boiling-heat till it has lost its glutinous character. It is then washed, dried, and ignited, dissolved in hydrochloric acid mixed with a little nitric acid, the copper precipitated by hydrosulphuric acid, and the filtrate, after boiling for a minute to expel the excess of that gas, mixed with boiling caustic potash to precipitate the cobalt.*—2. Instead of adding the oxide of mercury, the solution containing the mixed cyanides may, after cooling,

* Ann. Ch. Pharm. lxv. 244.

be supersaturated with chlorine, the precipitate of cyanide of nickel thereby produced being continually redissolved by caustic potash or soda. The chlorine produces no change on the cobalticyanide of potassium, but decomposes the nickel-compound, the whole of the nickel being ultimately precipitated in the form of black sesquioxide.*

Liebig's first method† which consisted in treating the solution of the mixed cyanides with excess of hydrochloric or sulphuric acid, whereby the nickel was precipitated as cobalticyanide of nickel, leaving a solution of pure cobalticyanide of potassium, has been found, both by himself and others, not to give perfectly satisfactory results. The method by oxalic acid (p. 75.), and the precipitation of nickel from an ammoniacal solution of the two metals by potash (p. 76.) are not sufficiently accurate for quantitative analysis.

F. Claudet proposes to separate cobalt from nickel and other metals in the form of the ammonio-compound described on page 70., that compound being very insoluble, while corresponding compounds of the other metals do not appear to be formed under the same circumstances.

The separation of cobalt from nickel (also from zinc and the previously described metals) may likewise be effected by means of St. Evre's yellow compound, which is regarded by A. Stromeyer as a nitrite of cobaltic oxide and potash (p. 65.). The solution containing the mixed metals is diluted with water till about 300 parts of water are present to 1 part of protoxide of cobalt; a somewhat concentrated solution of nitrite of potash ‡ then added, and a sufficient quantity of acetic acid to redissolve any precipitated carbonates; and the

* Ann. Ch. Pharm. lxxxvii. 128. † Ibid. xli. 291.

‡ The nitrite of potash is prepared by fusing 1 part of nitre in contact with 2 parts of metallic lead, first at a low and then at a bright-red heat, exhausting the cooled mass with water, precipitating a small quantity of lead by carbonic acid, and then by sulphide of ammonium, evaporating to dryness, and heating to the melting-point to decompose any hyposulphite of potash that may have been formed.

solution left to stand for 12 to 24 hours in a covered vessel, then filtered and washed, first with acetate of potash, afterwards with alcohol. The precipitate contains all the cobalt in the form of the above-mentioned salts, and none of the other metals.*

SECTION V.

ZINC.

32·52; Zn. *or Eq.* 406·6.

The principal ores of zinc are *calamine,* or the carbonate, a pulverulent mineral generally of a reddish or flesh colour, and *zinc-blende,* a massive mineral of an adamantine lustre, and often black. The oxide, from the carbonate or from the calcined sulphide, is mixed with about $\frac{3}{4}$ of its weight of carbonaceous matter, and heated to a low white heat in retorts, or similar vessels of earthenware or iron. The zinc is then reduced and volatilised, and condenses in the colder part of the apparatus.

In Silesia, the mixture of zinc-oxide and charcoal, or coke, is heated in muffles (Fig. 4.) 3 feet long and 18 inches high,

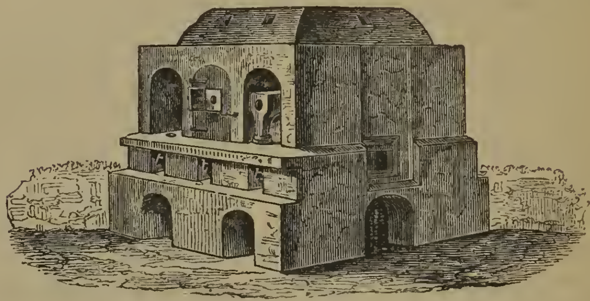
Fig. 4.

six of which are laid in one furnace (Fig. 5.), three side by side. The evolved mixture of carbonic oxide and zinc-vapour passes from the upper and fore part of the muffles M, through

* A. Stromeyer, Ann. Ch. Pharm. xcvi. p. 218.; see also Liebig and Kopp's Jahresbericht, 1854, p. 357.

a knee-shaped channel *b c d*, and the zinc condenses therein and drops down from the lower aperture *d* into the reservoirs *t* (Fig. 5.) placed beneath.

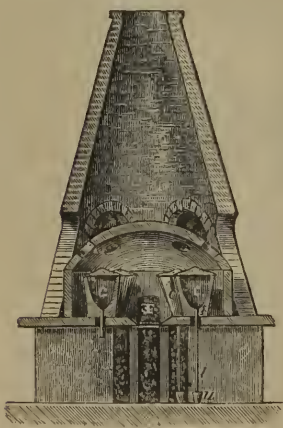
Fig. 5.



Part of the zinc-vapour, and likewise some cadmium-vapour, escapes uncondensed, together with the carbonic oxide gas, and burns in the air, producing the substance called *Silesian zinc-flowers*. Silesia furnishes the greater part of the zinc used in the arts.

In Belgium, the reduction is performed in earthenware tubes, laid side by side; and the zinc as it condenses in the fore part of these tubes, is scraped out from time to time in the liquid state.

Fig. 6.



In England, a number of cast-iron pots are arranged in a circle in the furnace (Fig. 6.). Through the bottom of each of these pots, there passes an iron tube *t t'*, which is continued downwards through an aperture in the bottom of the furnace. The upper end of the tube is stopped with a plug of wood, which is charred during the operation, and becomes sufficiently porous to allow

the passage of the zinc-vapour, but at the same time prevents the solid matter from falling through. Each pot is fitted with a cover well luted with clay. The fire-place F, is in the middle. The distilled zinc condenses in the tubes $t\,t'$, and falls in drops into a receiver u, placed beneath. This process is called *destillatio per descensum.*

Zinc may be purified by a second distillation in a porcelain retort; but the first portions of that metal which come over should be rejected, as they generally contain cadmium and arsenic.

Zinc is a white metal, with a shade of blue, capable of being polished and then assuming a bright metallic lustre. It is usually brittle, and its fracture exhibits a crystalline structure. But zinc, if pure, may be hammered into thin leaves, at the usual temperature; and commercial zinc, which is impure and brittle at a low temperature, acquires the same malleability between 210° and 300°: it may then be laminated; and the metal is now consumed in the form of sheet zinc for a variety of useful purposes. At 400° it again becomes brittle, and may be reduced to powder in a mortar of that temperature. The density of cast zinc is 6·862, but it may be increased by forging to 7·21. Its point of fusion is 773° (Daniell). At a red heat, zinc rises in vapour and takes fire in the air, burning with a white flame like that of phosphorus; the white oxide produced is carried up mechanically in the air, although itself a fixed substance. Laminated zinc is a valuable substance, from its little disposition to undergo oxidation. When exposed to air or placed in water, its surface becomes covered with a grey film of suboxide, which does not increase; this film is better calculated to resist both the mechanical and chemical effects of other bodies than the metal itself, and preserves it. Zinc dissolves with facility in dilute hydrochloric, sulphuric and other hydrated acids, by substitution for hydrogen. In contact

with iron, it protects the latter from oxidation in any saline fluid.

Zinc appears to form three oxides, the suboxide above referred to, the protoxide, and a peroxide, which last is produced when the hydrated protoxide is acted upon by a solution of peroxide of hydrogen; but of these, the first and last have not been studied, and the protoxide is, therefore, the only well known oxide of zinc.

Protoxide of zinc; ZnO; 40·52 *or* 506·6.—This oxide may be obtained, in the form of an anhydrous white powder, by the combustion of the metal in a stoneware crucible, or as a white hydrate, by precipitation from its salts by an alkali. It is of a yellow colour at high temperatures, but becomes colourless again on cooling. By the oxidation of zinc in air and water, without access of carbonic acid, a hydrate, $3ZnO + HO$, has been obtained in crystalline needles (Mitscherlich).

Oxide of zinc combines with acids and forms salts, which are colourless, like those of magnesia. *Caustic alkalies* form with zinc-salts a white gelatinous precipitate of the hydrated oxide, soluble in excess of the alkali. *Carbonate of potash* or *soda* throws down white carbonate of zinc, insoluble in excess; *carbonate of ammonia,* the same precipitate, soluble in excess. *Ferrocyanide of potassium,* and the *alkaline phosphates* and *arseniates,* also form white precipitates. Zinc-salts containing a strong acid in excess, are not affected by hydrosulphuric acid, but give a white hydrated sulphide with *alkaline sulphides.* A solution of acetate of zinc is readily decomposed by hydrosulphuric acid.

The native *sulphide of zinc,* or *zinc-blende,* ZnS, crystallises in octohedrons. Its colour is variable, being sometimes yellow, red, brown, or black.

Chloride of zinc, ZnCl, is produced by the combustion of zinc in chlorine, and by dissolving the metal in hydrochloric acid. It is fusible at 212°, volatile at a red heat, and perhaps the most deliquescent of salts. *Chloride of zinc-ammonium,*

$NH_3Zn.Cl$, is obtained, according to Ritthausen, in white prismatic crystals, when zinc and copper, or zinc and silver, are placed in contact in a solution of sal-ammoniac, or by the action of zinc on a solution of sal-ammoniac containing chloride of copper.

Iodide of zinc is formed by digesting iodine, zinc, and water together, and resembles the chloride. The compound $ZnI.2NH_3$, or $N\overbrace{H_2(NH_4)}Zn.I$, forms crystals belonging to the rhombic system (Rammelsberg).

The neutral *carbonate of zinc* forms the ore called calamine. When precipitated by an alkaline carbonate, the salts of zinc, like those of magnesia, yield the neutral carbonate in combination with hydrated oxide, $2(ZnO.CO_2) + 3(ZnO.HO)$. The mineral substance, *zinc-bloom*, is of the same composition. Precipitated in the cold, the carbonate is $ZnO.CO_2 + 2(ZnO.HO)$, but is contaminated with sulphate of soda (Mitscherlich).

Sulphate of zinc, White vitriol, $ZnO.SO_3 + 7HO$.—This salt is formed by the oxidation of the native sulphide at high temperatures, or by dissolving the metal in dilute sulphuric acid. It crystallises in colourless prismatic crystals, containing 7 eq. of water, the form of which is a right rhombic prism. This, like all the other magnesian sulphates, gives up 6 eq. of its water at about 212°, while the seventh or constitutional equivalent requires a heat of 400° to expel it. The crystals are soluble in $2\frac{1}{2}$ times their weight of water, at the usual temperature, and fuse in their water of crystallisation when heated. The salt also crystallises above 86°, with 6 eq. of water, in oblique rhombic prisms (Mitscherlich). According to Kühn, another hydrate is formed and precipitated as a white powder, containing 2 eq. of water, when a concentrated solution of sulphate of zinc is mixed with oil of vitriol. Sulphate of zinc forms the usual double salt with sulphate of potash, $ZnO.SO_3 + KO.SO_3 + 6HO$. The double sulphate of zinc and

soda contains 4 atoms of water, $ZnO.SO_3+NaO.SO_3+4HO$. It is formed by a singular decomposition (I. 228.). When a solution of the sulphate is mixed with a quantity of alkali less than sufficient for complete precipitation, a *subsulphate of zinc* precipitates, which, according to the analyses of several chemists, contains 4 eq. of oxide of zinc to 1 eq. of sulphuric acid, besides water. A concentrated solution of sulphate of zinc dissolves the preceding subsalt, and, when saturated, contains a compound of 1 eq. of acid and 2 eq. of base, according to Schindler, and does not crystallise. From this solution, Schindler obtained the former insoluble subsalt with two different proportions of water, in long crystalline needles, containing 10HO, by spontaneous evaporation of the solution, and in brilliant crystalline plates containing 2HO, which were deposited on boiling the solution. By diluting the same solution with a large quantity of water, he also obtained another subsalt, as a light bulky precipitate, which contained 1 eq. of acid, 8 eq. of oxide of zinc, and 2 eq. of water. The insoluble matter, which precipitates when sulphate of zinc-ammonium $(NH_3Zn)O.SO_3$ is thrown into water, is considered by Kane as a third subsulphate of zinc, containing 1 eq. of acid, 6 eq. of oxide of zinc, and 10 eq. of water. All these subsulphates afford neutral sulphate of zinc to water, after being heated to redness; so that, whatever their constitution may be when hydrated, it is certainly different from what it is in their anhydrous condition.

Nitrate of zinc, $ZnO.NO_5+6HO$, is very soluble in water, and moderately deliquescent.

Phosphate of zinc, $ZnO_2.HO.PO_5 + 2HO$, is obtained in minute silvery plates, which are nearly insoluble, on mixing dilute solutions of phosphate of soda and sulphate of zinc.

Silicate of zinc is found as a crystalline mineral, which has received the name of the electrical oxide of zinc, because it acquires, like the tourmalin, a high degree of electrical

polarity when heated. It contains water, and may be represented by the formula $2(3ZnO.SiO_3)+3HO$.

The most important *alloys of zinc* are those with copper, which form the varieties of brass. Zinc also combines readily with iron, and is contaminated by that metal, when fused in an iron crucible.

ESTIMATION OF ZINC, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Zinc is precipitated from its solutions by carbonate of soda, which, when added in excess and boiled with the solution, throws down carbonate of zinc. It is best, however, to pour the zinc-solution into the hot solution of the alkaline carbonate, because, in that case, we may be sure of not forming a basic salt. If the zinc-solution contains ammoniacal salts, it must be boiled with a quantity of carbonate of soda sufficient to decompose those salts; then evaporated to dryness; the residue treated with a large quantity of water to dissolve out the soluble salts; and the carbonate of zinc collected on a filter and well washed with hot water. The evaporation should be conducted as quickly as possible. The carbonate of zinc, when dried and ignited, yields oxide of zinc containing 80·26 per cent. of the metal.

In separating zinc from other metals, it is often necessary to precipitate by sulphide of ammonium. If the solution is acid, it must be previously neutralised by ammonia. The precipitate must not be thrown on the filter immediately, but left to settle down completely, after which the clear liquid must first be passed through the filter, and then the precipitate thrown on it. If this precaution be neglected, the sulphide of zinc will stop up the pores of the filter. The precipitate is washed with water containing a little sulphide of ammonium; then dissolved in hydrochloric acid; the solution

boiled to drive off the hydrosulphuric acid; and the zinc precipitated by carbonate of soda as above.

Zinc is separated from the *alkalies* and *alkaline earths* (baryta, strontia, and lime) by means of sulphide of ammonium. In the case of the alkaline earths, however, great care must be taken to prevent the ammoniacal liquid from absorbing carbonic acid from the air, as that would occasion a precipitation of the earth in the form of carbonate. For this purpose, the filtration must be effected as quickly as possible, and the liquid well protected from the air. The separation of zinc from *baryta* may also be effected by sulphuric acid, and from *lime* by oxalate of ammonia.

From *magnesia*, zinc may be separated by sulphide of ammonium, a sufficient quantity of chloride of ammonium being previously added to prevent the precipitation of the magnesia. Or the separation may be effected by converting the zinc and magnesia into acetates, and precipitating the zinc as sulphide by hydrosulphuric acid.

The separation of zinc from *alumina* and *glucina* may also be effected by converting the two bases into acetates and precipitating the zinc by hydrosulphuric acid; or by dissolving in potash, and precipitating the zinc by hydrosulphuric acid; but the former method is to be preferred.

The conversion into acetates and precipitation by hydrosulphuric acid likewise serves to separate zinc from *zirconia, yttria, thorina,* and *manganese*. The separation from manganese may also be effected by converting the two metals into chlorides, passing chlorine gas through the solution to convert the manganese into bioxide, and completing the precipitation of the latter by carbonate of baryta.

From *iron,* zinc may be separated by ammonia, or better by succinate of ammonia, the same precautions being used as in the separation of iron from manganese by the same method (p. 58.). The iron (in the state of sesquioxide) may also be precipitated by carbonate of lime or carbonate of baryta.

From *cobalt* and *nickel,* zinc is separated by dissolving the oxides of both metals in *excess* of acetic acid, and precipitating the zinc by hydrosulphuric acid. Nickel and cobalt are completely precipitated by hydrosulphuric acid from the neutral solutions of their acetates, but not when a considerable excess of acetic acid is present. But in separating zinc from cobalt and nickel in this manner, a small quantity of the latter metals is generally precipitated with the zinc towards the end of the process, the precipitate then becoming greyish black. In that case it must be redissolved in hydrochloric acid, the chlorides converted into acetates, and the precipitation repeated. Another method of separation is to convert the metals into chlorides, and ignite the dry chlorides in a stream of hydrogen gas: the nickel or cobalt is then reduced to the metallic state, while the chloride of zinc remains unaltered, and may be dissolved out by water. (For the separation of cobalt from zinc, see also p. 80.)

In precipitating zinc from its acetic acid solution by hydrosulphuric acid, it is necessary that the solution be quite free from inorganic acids, which would interfere with the precipitation. This may be effected either by precipitating the metals with carbonate of soda, washing the precipitate and dissolving it in acetic acid, or by boiling the solution with excess of sulphuric acid to drive off the inorganic acids (if volatile) and decomposing the sulphate with acetate of baryta.

SECTION VI.

CADMIUM.

Eq. 55·74 *or* 696·77; Cd.

This metal is frequently found in small quantity, associated with zinc, and derives the name cadmium, applied to it by Stromeyer, from *cadmia fossilis,* a denomination by which the

common ore of zinc was formerly designated. In the process of reducing ores of zinc, the cadmium which they contain comes over among the first products of distillation, owing to its greater volatility. It may be separated from zinc, in an acid solution, by hydrosulphuric acid, which throws down cadmium as a yellow sulphide. This sulphide dissolves in concentrated hydrochloric acid, affording the chloride of cadmium, from which the carbonate may be precipitated by an excess of carbonate of ammonia. Carbonate of cadmium is converted by ignition into the oxide; and the latter yields the metal when mixed with one-tenth of its weight of pounded coal, and distilled in a glass or porcelain retort, at a low red heat.

Cadmium is a white metal, like tin, very ductile and malleable. It fuses considerably under a red heat, and is nearly as volatile as mercury. The density of cadmium, cast in a mould, is 8·604, after being hammered, 8·6944. Cadmium may be dissolved in the more powerful acids, by substitution for hydrogen, with the aid of heat; but nitric acid is its proper solvent.

Oxide of cadmium, CdO; 63·74 *or* 796·77.—The only known oxide of cadmium is obtained by the combustion of the metal, or by the ignition of its carbonate, as a powder of an orange colour, or as a white hydrate by precipitation from its salts by an alkali. Its density, in the anhydrous condition, is 8·183 (Herapath). By igniting the nitrate, the oxide is obtained in microscopic octohedrons, which are dark bluish black by reflected, and dark brown with a tinge of violet by transmitted light (Schüler). This oxide is soluble in ammonia, but not in its carbonate (differing in the last property from zinc and copper) nor in the fixed alkalies. Its salts are white, and greatly resemble those of zinc. They are precipitated of a fine yellow colour by hydrosulphuric acid.

Sulphide of cadmium is distinguished from sulphide of arsenic, which it resembles in colour, by being insoluble in potash and in sulphide of ammonium, and by sustaining a red

heat without subliming. A crystalline sulphide is obtained by fusing 1 part of the precipitated sulphide with 5 parts of carbonate of potash and 5 parts of sulphur; or by passing dry hydrosulphuric acid gas over strongly-heated chloride of cadmium.

Chloride of cadmium forms a crystalline hydrate, containing $CdCl + 2HO$. It also forms crystalline compounds with the chlorides of ammonium, potassium, sodium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. A solution of chloride of cadmium, mixed with excess of ammonia, yields by spontaneous evaporation the compound NH_2CdCl (C. v. Hauer).

The same ammoniacal solution treated with excess of hydrochloric acid deposits crystalline crusts, which, according to Schüler, contain $CdCl.3NH_3$ or $NH\overbrace{(NH_4)_2Cd}.Cl$. Sulphurous acid gas passed through the ammoniacal solution throws down a white crystalline precipitate containing $CdO.SO_2 + NH_4O.SO_2$ (Schüler).

Iodide of cadmium forms a crystalline compound with water.

Bromide of cadmium mixed in equivalent quantity with bromide of potassium in solution, yields crystals, first of $2CdBr.KBr + 2HO$, afterwards of $CdBr.2KBr$ (C. v. Hauer).

Sulphate of cadmium forms efflorescent crystals containing $CdO.SO_3 + 4HO$ (Stromeyer). According to Kühn and Von Hauer, an acid solution of the salt concentrated at the boiling heat, deposits nodular crystals, which contain $CdO.SO_3 + HO$, and give off their water at 212°. The crystals obtained by evaporation at ordinary temperatures contain $3(CdO.SO_3) + 8HO$, give off nearly 3 eq. water at 212°, and the rest at a low red heat (C. v. Hauer). Sulphate of cadmium forms with sulphate of potash the compound $CdO.SO_3 + KO.SO_3 + 6HO$, and similar double salts with the sulphates of soda and ammonia.

Several definite *alloys of cadmium* have been formed. At a red heat, 100 parts of platinum retain 117·3 parts of cadmium,

giving a compound = Cd_2Pt: 100 parts of copper retain, at a red heat, 82·2 of cadmium, which approaches nearly to the proportion of $CdCu_2$. Cadmium forms an amalgam with mercury, which crystallises in octohedrons, and consists of 21·74 parts of cadmium, and 78·26 of mercury, $CdHg_2$.

Estimation of cadmium, and method of separating it from the preceding metals. — Cadmium is best precipitated from its solutions by carbonate of soda; it is thereby obtained as a carbonate, which by ignition yields the brown oxide containing 87·45 per cent. of the metal.

From all the preceding metals cadmium may be separated by hydrosulphuric acid; the sulphide of cadmium being then dissolved by nitric acid, and the metal precipitated by carbonate of soda as above.

SECTION VII.

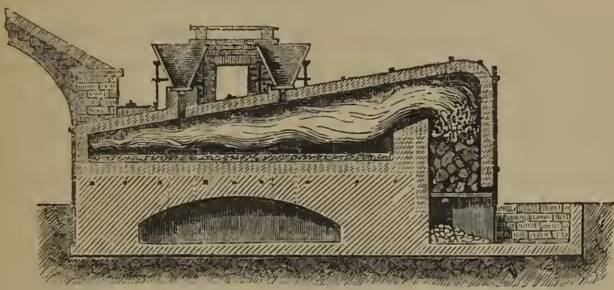
COPPER.

Eq. 31·66 *or* 395·7; Cu (*cuprum*).

Copper, if not the most abundant, is certainly one of the most generally diffused of the metals. Its ores are often accompanied by metallic copper, crystallised in cubes or octohedrons. Very large masses of native copper have been found near Lake Superior in North America, one of which weighed 2200 pounds; in the Cliff mine, on the Eagle river, a mass has been found weighing 50 tons. Native copper is also found in considerable quantities in the decomposed basalt of Rheinbreitenbach, near Reesk in Hungary, and near Harlech, North Wales. The richest mines of this country are those in Cornwall and Anglesea. The common ore of this metal is *copper pyrites*, a compound of subsulphide of copper and sesquisulphide of iron, or a sulphur-salt, $CuS + Fe_2S_3$, but in

which the two sulphides are also found in other proportions, and which often contains an admixture of the bisulphide of iron. Few metallurgic processes require more skill and attention than the extraction of copper from this ore. The ore is first roasted at a high temperature in a reverberatory or flame-furnace (Fig. 7.), whereby the sulphide of iron is in great part

Fig. 7.



converted into oxide, while the sulphide of copper remains unaltered. The product of this operation is then strongly heated with silicious sand, which combines with the oxide of iron, forming a fusible slag, and separates from the heavier copper compound. This operation is performed in a reverberatory furnace similar to the former, but of smaller dimensions. These processes are several times repeated, whereby the quantity of iron is continually diminished, and the sulphide of copper begins to decompose, giving it up its sulphur and absorbing oxygen; the temperature is then raised high enough to reduce the resulting oxide by the aid of carbonaceous matter. The *coarse copper* thus obtained, containing from 80 to 90 per cent. of copper, is then melted under the action of a strong blast of air, to complete the expulsion of volatile matter, and the copper is partially oxidised. Lastly, to free it from oxide, which renders it brittle, it is again melted with its surface well covered with charcoal, and a pole of birchwood is thrust into it; this causes considerable ebullition, the oxide being reduced

by the carbonaceous matter, and carbonic acid escaping. Samples of the metal are taken out from time to time, and tested by the hammer, the process being discontinued as soon as the right degree of toughness is attained. If the *poling* is continued too long, the copper takes up carbon, and then becomes even more brittle than in its former oxidised state: it is then said to be *over-poled,* and must be again melted in contact with the air to burn away the carbon.*

Copper is the only metal of a red colour. The crystals of native copper, and of that obtained in the humid way by precipitation with iron, belong to the regular system; but the crystals which form in the cooling of melted copper were found by Seebeck to be rhomboïdal, and to have a different place in the thermo-electric series from the other crystals. The density of copper when cast is about 8·83, and when laminated or forged 8·95 (Berzelius). It is less fusible than silver, but more so than gold, its point of fusion being 1996° (Daniell). It is one of the most highly malleable metals, and in tenacity is inferior only to iron. It has much less affinity for oxygen than iron, and decomposes water only at a bright red heat, and to a small extent. In damp air, it acquires a green coating of subcarbonate of copper, and its oxidation is remarkably promoted by the presence of acids. The weaker acids, such as acetic, have no effect upon copper, unless with the concurrence of the oxygen of the air, when the copper rapidly combines with that oxygen, and a salt of the acid is formed. Copper scarcely decomposes the hydrated acids by displacing hydrogen; when boiled in hydrochloric acid, it disengages only the smallest traces of that gas. But hydrogen does not precipitate metallic copper from solution. Copper acts violently on nitric acid, occasioning its decomposition, with evolution of nitric oxide, and dissolving as a nitrate.

* A minute account of the process of copper-smelting as practised at Swansea, has lately been given by Mr. Napier, in the "Philosophical Magazine," 4th Series, vols. iv. and v.

Dioxide of copper, Red oxide of copper, Cuprous oxide, Cu_2O; 71·32 or 891·4.—This degree of oxidation is better marked in copper than in any other metal of the magnesian class. The dioxide of copper is found native in octohedral crystals, and may be prepared artificially by heating to redness, in a covered crucible, a mixture of 5 parts of the black oxide of copper with 4 parts of copper-filings. It is a reddish-brown powder, which undergoes no change in the air. The surface of vessels of polished copper is often converted into red oxide, or bronzed, to enable them to resist the action of air and moisture: this is done by covering them with a paste of sesquioxide of iron, heating to a certain point, and afterwards cleaning them, to remove the oxide of iron; or otherwise, by means of a boiling solution of acetate of copper.

Dilute acids decompose red oxide of copper, dissolving the protoxide, and leaving metallic copper. Undiluted hydrochloric acid dissolves the red oxide, without decomposition, or rather forms a corresponding chloride of copper, Cu_2Cl, which is soluble in hydrochloric acid. The hydrated alkalies precipitate hydrated cuprous oxide from that solution, of a lively yellow colour, which changes rapidly in air from absorption of oxygen.

Cuprous oxide is also formed when copper is placed in a dilute solution of ammonia containing air, and is dissolved by the alkali. If the ammonia has been corked up in a bottle with copper for some time, the liquid is colourless; but on pouring it out in a thin stream, it immediately becomes blue, by absorbing oxygen. The liquid may be again deprived of colour by returning it to the bottle, and closing it up, in contact with the metal. Cuprous oxide is also readily obtained by the reducing action of glucose (grape-sugar) on the protoxide or its salts. When a solution of 1 part of common sulphate of copper and 1 part of glucose is mixed with a sufficient quantity of caustic potash or soda to redissolve the precipitate first formed, and the liquid gently warmed, cuprous oxide is

abundantly precipitated in the form of a yellowish-red crystalline powder. Cane-sugar produces the same effects, but more slowly, apparently because it must first be converted into glucose.

Compounds have been obtained of cuprous-oxide with several acids, particularly with sulphurous acid, the sulphite forming a double salt with sulphite of potash, $Cu_2O.SO_2 + 2(KO.SO_2)$ (Muspratt); also with hyposulphurous, sulphuric, carbonic and acetic acids. When fused with vitreous matter, cuprous oxide gives a beautiful ruby-red glass; but it is difficult to prevent the cuprous oxide from absorbing oxygen, in which case the glass becomes green.

Hydride of copper, Cuprous hydride, Cu_2H. — When a solution of cupricsulphate and hypophosphorous acid is heated not above 158°, this compound is deposited as a yellow precipitate, which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and when treated with hydrochloric acid, is converted into dichloride of copper, with evolution of a double quantity of hydrogen, the acid in fact giving up its hydrogen as well as the copper-compound (Wurtz):

$$Cu_2H + HCl = Cu_2Cl + HH.$$

This action is very remarkable, inasmuch as metallic copper is scarcely acted upon by hydrochloric acid. It appears to arise from the two atoms of hydrogen contained in the acid and the hydride being in opposite states, the former being basylous or positive, the latter chlorous or negative, and so disposed to *combine together,* just as the hydrogen of the hydrochloric acid combines under similar circumstances with the oxygen of the compound Cu_2O. The reduction of certain metallic oxides by peroxide of hydrogen affords another example of the same kind of action.

Disulphide of copper, Cuprous sulphide, Cu_2S, forms the mineral *copper-glance,* and is also a constituent of copper

pyrites. It is a powerful sulphur-base. Copper-filings, mixed with half their weight of sulphur, unite, when heated, with intense ignition, and form this disulphide.

Dichloride of copper, *Cuprous chloride*, Cu_2Cl, may be prepared by heating copper-filings with twice their weight of corrosive sublimate. It was obtained by Mitscherlich in tetrahedrons, by dissolving in hydrochloric acid the dichloride of copper formed on mixing solutions of the protochlorides of copper and tin, and allowing the concentrated solution to cool. Dichloride of copper so prepared is white, insoluble in water, soluble in hydrochloric acid, but precipitated by dilution. It is dissolved by a boiling solution of chloride of potassium, and the resulting solution, if allowed to cool in a close vessel, yields large octohedral crystals of a double chloride: $Cu_2Cl.2KCl$; they are anhydrous. It is remarkable that the forms of this double salt, and of both its constituents, all belong to the regular system.*

When finely-divided metallic copper is boiled in a saturated solution of sal-ammoniac, ammonia is evolved and a white salt formed, which crystallises in rhombic dodecahedrons: it contains $NH_3.Cu_2Cl$, and may be regarded as a dichloride of copper and cuprammonium $\left.\begin{matrix}NH_3Cu\\Cu\end{matrix}\right\}Cl$. A solution of this salt exposed to the air yields blue crystals of the compound $NH_3.Cu_2Cl + NH_3CuCl + HO$; and the mother-liquor, after further exposure to the air, contains the salt $NH_3.CuCl + NH_4Cl$, which at a lower temperature crystallises in large cubes (Ritthausen).

Diniodide of copper, *Cuprous iodide*, Cu_2I, is a white insoluble precipitate, obtained on mixing a solution of 1 part of sulphate of copper and $2\frac{1}{4}$ parts of protosulphate of iron, with a solution of iodide of potassium.

Dicyanide of copper, *Cuprous cyanide*, Cu_2Cy.—Obtained as a white curdy precipitate on adding hydrocyanic acid or

* Mitscherlich in Poggendorff's Annalen, xlix. 401., 1840.

cyanide of potassium to a solution of dichloride of copper in hydrochloric acid, or to a solution of protochloride of copper mixed with sulphurous acid. It forms a colourless solution with ammonia, and a yellow solution with strong hydrochloric acid, from which it is precipitated by potash.

Dicyanide of copper unites with the cyanides of the alkali- and earth-metals, and with the cyanides of manganese, iron, zinc, cadmium, lead, tin, uranium, and silver, forming double salts, some of which have the composition $MCy.Cu_2Cy$, others $3MCy.Cu_2Cy$ (the symbol M denoting a metal).

Cuproso-cupric cyanide, $Cu_2Cy.CuCy$, is obtained as a green hydrate by adding hydrocyanic acid or cuproso-potassic cyanide, $KCy.Cu_2Cy$, to sulphate of copper. It forms three compounds with ammonia, viz., $NH_3.Cu_3Cy_2.HO$, obtained by adding cyanide of ammonium to a protosalt of copper, and the compounds $2NH_3.Cu_3Cy_2$ and $3NH_3.Cu_3Cy_2$, formed by the action of ammonia on the first compound.

Cuprous hyposulphite, $Cu_2O.3S_2O_2 + 2HO$, separates in microscopic needles, having a golden lustre, on adding a saturated solution of hyposulphite of soda to a concentrated solution of cupric sulphite, till a deep yellow colour is produced. It dissolves in aqueous sal-ammoniac, and the solution deposits the compound $Cu_2O.3S_2O_2 + NH_3CuCl + HO$. (C. v. Hauer).

Cuprous sulphite is said by some chemists to be obtained in a definite state by the action of sulphurous acid on cupric oxide; but according to Rammelsberg and Péan de St. Gilles, it exists only in combination with cupric sulphite, forming the compound $Cu_2O.SO_2 + CuO.SO_2$, which crystallises with 3 and 5 eq. of water,—and with the sulphites of the alkalies. By treating dichloride of copper with excess of sulphite of ammonia, prismatic crystals are formed containing $Cu_2O.SO_2 + 7(NH_4O.SO_2) + 10$ Aq.; and by saturating the solution of this salt with sulphurous acid, the salt $Cu_2O.S_2O_2 + NH_4O.SO_3$ is obtained. A concentrated solution of sulphite

of ammonia and cupric sulphate saturated with sulphurous acid gas, yields light green crystals containing $(Cu_2O.SO_2 + NH_4O . SO_2) + (Cu_2O . SO_2 + CuO . SO_2) + 5$ aq. Corresponding double salts are formed by the sulphites of potash and soda, but they are very unstable.

Protoxide of copper, Black oxide of copper, Cupric oxide, CuO; 495·7 or 39·66.—The base of the ordinary salts of copper, or cupric salts. It is formed by the oxidation of copper at a red heat, but is generally prepared by igniting the nitrate of copper. It is black like charcoal, and fuses at a high temperature. This oxide is remarkable for the facility with which it is reduced, at a low red heat, by hydrogen and carbon, which it converts into water and carbonic acid. It is this property which recommends oxide of copper for the combustion of organic substances, in close vessels, by which their ultimate analysis is effected.

Oxide of copper is a powerful base. Its salts, the *cupric* salts, are generally blue or green, when hydrated, but white when anhydrous. Although neutral in composition, they have a strong acid reaction. They are poisonous; but their effect upon the animal system is counteracted in some degree by sugar. Liquid albumen forms insoluble compounds with these salts, and is an antidote to their poisonous action. Copper is separated in the metallic state from its salts by zinc, iron, lead, and the more oxidable metals, which are dissolved, and take the place of the former metal.

Potash or *soda* added to the solution of a cupric salt, throws down at first a blue precipitate of hydrated cupric oxide, which, however, on agitation, takes up a portion of the undecomposed salt, and forms with it a green basic salt. An excess of the alkali throws down the hydrated oxide in bulky blue flakes, which, on boiling the mixture, collect together in the form of a black powder, consisting of the anhydrous oxide. This reaction is greatly modified by the presence of fixed or-

ganic substances, such as sugar, tartaric acid, &c. In a solution of sulphate of copper, containing such substances in sufficient quantity, potash either produces no precipitate, or one which is quickly redissolved, forming a blue solution; and from this solution, when boiled, the copper is sometimes wholly precipitated as red or yellow cuprous oxide, as when grape-sugar is present,—or partially, as with cane-sugar, or not at all, as with tartaric acid. *Ammonia*, added by degrees, and with constant agitation, to the solution of a cupric salt, first throws down a green basic salt, and afterwards the blue hydrate: an excess of ammonia dissolves the precipitate, forming a deep blue solution. A copper solution diluted so far as to be colourless, becomes distinctly blue on the addition of ammonia. The blue colour thus produced is still visible, according to Lassaigne, in a solution containing 1 part of copper in 100,000 parts of liquid. *Carbonate of potash* or *soda* throws down, with evolution of carbonic acid, a greenish blue precipitate of a basic carbonate of copper, which on boiling is converted into the black oxide. *Carbonate of ammonia* produces the same precipitate, but when added in excess, dissolves it abundantly, forming a blue solution. *Hydrosulphuric acid* and solutions of *alkaline sulphides* throw down a brownish black precipitate of protosulphide of copper, insoluble in sulphide of potassium or sodium, slightly soluble in sulphide of ammonium. *Ferrocyanide of potassium* forms with cupric salts a deep chocolate-coloured precipitate of ferrocyanide of copper. To very dilute solutions it imparts a reddish colour, which is even more delicate in its indications than the ammonia reaction, being still visible in a solution containing 1 part of copper in 400,000 parts of liquid, according to Lassaigne, and in 1,000,000 parts, according to Sarzeau. Ferrocyanide of copper dissolves in aqueous ammonia, and reappears when the ammonia is evaporated. This reaction serves to detect extremely small quantities of copper, even when associated with other metals. Thus, if a solution

containing copper and iron be treated with excess of ammonia, a few drops of ferrocyanide of potassium added, the liquid filtered, and the filtrate left to evaporate in a small white porcelain capsule, ferrocyanide of copper will be left behind, exhibiting its characteristic red colour (Warington). Salts of copper impart a green colour to flame. The black oxide of copper dissolves by fusion in a vitreous flux, and produces a green glass. Any compound of copper fused with borax in the oxidising flame of the blowpipe forms a transparent glass, which is green while hot, but assumes a beautiful blue colour when cold. In the reducing flame, the glass becomes opaque, and covered on the surface with liver-coloured streaks of cuprous oxide, or metallic copper. This last reaction is somewhat difficult to obtain, especially when the quantity of copper is small, but it may always be ensured by fusing a small piece of metallic tin in the bead. Copper salts mixed with carbonate of soda or cyanide of potassium, and heated on charcoal before the blowpipe, yield metallic copper.

Thénard obtained a higher oxide of copper, CuO_2, by the action of diluted bioxide of hydrogen on the hydrated protoxide of copper.

Chloride of copper, cupric chloride, CuCl, is obtained by dissolving the black oxide in hydrochloric acid. Its solution is green when concentrated, but blue when more dilute, and the salt forms blue prismatic crystals, containing two atoms of water. It combines with chloride of potassium, and more readily with chloride of ammonium, forming the double salts KCl.CuCl + 2HO, and $NH_4Cl.CuCl + 2HO$. Another chloride of copper and ammonium, containing $NH_4Cl.2CuCl + 4HO$, is obtained in fine bluish-green crystals, by mixing the solutions of 1 eq. sal-ammoniac and 2 eq. chloride of copper.

Chloride of copper likewise combines with ammonia, forming the three following compounds:—*a.* $3NH_3.CuCl$. This compound is obtained by saturating dry protochloride of

copper with ammoniacal gas: it forms a blue powder.—*b*. $2NH_3.CuCl$. Formed by passing ammoniacal gas through a hot saturated solution of protochloride of copper, till the precipitate first formed is completely redissolved. During this process, the liquid is kept almost boiling by the heat developed by the absorption of the gas; and the resulting solution yields, on cooling, small dark blue octohedrons and square prisms with four-sided summits.—*c*. $NH_3.CuCl$. Obtained by heating *a* or *b* to 300°, or by saturating dry chloride of copper, at a high temperature, with ammoniacal gas. Forms a green powder. The compound *c* may also be regarded as *chloride of cuprammonium*, $NH_3Cu.Cl$, or *hydrochlorate of cupramine*, $NH_2Cu.HCl$, the base being ammonium or ammonia in which 1H is replaced by Cu. Similarly, *b* may be regarded as a *basic hydrochlorate of dicupramine*, $N_2H_5Cu.HCl$, the base being formed by the union of two atoms of ammonia into one, and the substitution therein of 1Cu for 1H. Lastly, *a* may be regarded as *basic hydrochlorate of tricupramine*, $N_3H_8Cu.HCl$; or again, *a* may be regarded as $N\overbrace{HAm_2Cu}.Cl$, and *b* as $N\overbrace{H_2AmCu}.Cl$.

Carbonates of copper.—When a salt of copper is precipitated by an alkaline carbonate, a hydrated subcarbonate is produced containing 2 eq. of oxide of copper to 1 eq. carbonic acid. It is a pale blue bulky precipitate, which becomes denser and green when treated with boiling water. It is used as a pigment, and known as *mineral green*. The beautiful native green carbonate of copper, *malachite*, is of the same composition, $CuO.CO_2 + CuO.HO$. The finely crystallised *blue copper ore* is another subcarbonate. It may be represented as the neutral hydrated carbonate of copper, in combination with a similar carbonate of copper, in which the constitutional water is replaced by oxide of copper:

$$\begin{cases} CuO.CO_2 + HO. \\ CuO.CO_2 + CuO. \end{cases}$$

In the green carbonate, the constitutional water of the neutral

carbonate of copper is replaced by hydrate of copper. The neutral carbonate of copper itself, of which the formula would be $CuO.CO_2 + HO$, is unknown. According to Thomson*, the anhydrous subcarbonate $2CuO . CO_2$, occurs in the form of *mysorine*, which contains also ferric oxide and silica.

Sulphate of copper, Cupric sulphate, Blue vitriol, $CuO.SO_3.HO + 4HO$; 79·66 *or* 995·7 + 562·5.—This salt may be formed by dissolving copper in sulphuric acid diluted with half its bulk of water, with ebullition; the metal is then oxidated with formation of sulphurous acid. But the sulphate of copper is more generally prepared, on the large scale, by the roasting and oxidation of sulphide of copper; or by dissolving in sulphuric acid the oxide formed by exposing sheets of metallic copper to air at a red heat. It forms large rhomboïdal crystals of a sapphire-blue colour, containing 5 eq. of water, which lose their transparency in dry air: they are soluble in four times their weight of cold, and twice their weight of boiling water. Like the other soluble salts of copper, the sulphate has an acid reaction; it is used as an escharotic. The water in this salt may be reduced to 1 eq. at 212°; above 400° the salt is anhydrous and white. Although sulphate of copper does not crystallise alone with 7HO, yet, when mixed with the sulphates of magnesia, zinc, nickel, and iron, it crystallises along with these isomorphous salts in the form of sulphate of iron. At a strong red heat it melts and loses acid.

The anhydrous sulphate absorbs $2\frac{1}{2}$ eq. of ammonia, and forms a light powder of a deep blue colour (H. Rose). When ammonia is added to a solution of sulphate of copper, an insoluble subsulphate is first thrown down, which is redissolved as the addition of ammonia is continued, and the usual deep azure-blue ammoniacal solution formed. The ammoniacal sulphate may be obtained in beautiful indigo-blue crystals, by passing

* Outlines of Mineralogy.

a stream of ammoniacal gas into a saturated hot solution of the sulphate: it is $CuO.SO_3.HO + 2NH_3$ (Berzelius). These crystals lose 1 eq. ammonia and 1 eq. water at 390° (Kane), and are converted into a green powder, $CuO.SO_3 + NH_3$, or $(NH_3CuO).SO_3$; by the cautious application of a heat not exceeding 500°, the whole of the ammonia may be got rid of, and sulphate of copper quite pure remains behind. Sulphate of copper forms the usual double salts with sulphate of potash and with sulphate of ammonia. A saturated hot solution of the double sulphate of copper and potash allows a remarkable double subsalt to precipitate in crystalline grains, $KO.SO_3 + 3(CuO.SO_3) + CuO.HO + 3HO$. A corresponding seleniate is deposited, below the boiling point, and always in crystals. The ammoniacal and double salts of sulphate of copper may be represented thus:—

Sulphate of copper (blue vitriol) . . .	$CuO.SO_3,HO + 4HO$
Sulphate of copper and potash	$CuO.SO_3,(KO.SO_3) + 6HO$
Hydrated ammoniacal sulphate of copper	$CuO.SO_3,HO + 2NH_3$
Preceding salt dried at 300°	$(NH_3.CuO).SO_3$
Rose's ammoniacal sulphate	$CuO.SO_3 + (NH_3CuO)SO_3 + 4NH_3$
Do. heated to 350°	$CuO.SO_3 + (NH_3CuO)SO_3$

The hydrated ammoniacal sulphate may also be regarded as $\overbrace{NH_2(NH_4)Cu}.SO_4$; and Rose's ammoniacal sulphate as

$$\left.\begin{array}{l}\overbrace{NH_2(NH_4)Cu}\\ \overbrace{NH(NH_4)_2Cu}\end{array}\right\}2SO_4.$$

Several *subsulphates of copper* have been formed. By digesting hydrated oxide of copper in a solution of sulphate of copper, a green powder is obtained, of which the constituents are, according to Berzelius, $3CuO.SO_3 + 3HO$. The bluish-green precipitate which falls when ammonia is added to sulphate of copper, or potash added in moderate quantity to the same salt, contains, according to Kane's and Graham's analyses $4CuO.SO_3 + 4HO$. By a larger quantity of potash, Kane precipitated a clear grass-green subsulphate, containing

$8CuO.SO_3+12HO$. The last subsulphate loses exactly half its water at 300°.*

Nitrate of copper, $CuO.NO_5+3HO$, is formed by dissolving copper in nitric acid. It crystallises from a strong solution in blue prisms which contain 3 atoms of water, or in rhomboïdal plates which contain 6 atoms of water. This salt acts upon granulated tin, with nearly as much energy as hydrated nitric acid. A crystallised *ammoniacal nitrate of copper* is obtained by conducting a stream of ammoniacal gas into a saturated solution of nitrate of copper. It is anhydrous, and contains $NO_5.CuO + 2NH_3$ (Kane). It may be regarded as $N\overbrace{H_2(NH_4)Cu}.NO_6$.

Subnitrate of copper, $CuO.NO_5 + 3(CuO . HO)$, according to the analyses of Gerhardt, Gladstone†, and Kuhn‡, is a green powder, produced by the action of heat upon the neutral nitrate, at any temperature between 160° and 600°; or by adding to that salt a quantity of alkali insufficient for complete precipitation. When oxide of copper is drenched with the most concentrated nitric acid ($HO.NO_5$), it is this subsalt, singular as it may appear, which is formed, even when the acid is in great excess.

Oxalate of copper and potash is obtained by dissolving oxide of copper in binoxalate of potash; it crystallises with 2 and with 4 eq. of water.

Acetates of copper.—The *neutral acetate*, $CuO.(C_4H_3O_3)+HO$, or $C^4H^3CuO^4 + HO$, is obtained by dissolving oxide of copper in acetic acid. It forms fine crystals of a deep green colour, containing 1 eq. of water, which lose their transparency in air, and are soluble in 5 times their weight of boiling water. This salt, when it separates from an acid solution below 40°, also forms blue crystals containing 5HO

* Transactions of the Royal Irish Academy, vol. xix. p. 1.; or Ann. Ch. Phys. t. lxxii. p. 272.

† Chem. Soc. Mem. iii. 480.

‡ Arch. Pharm. [2.], l. 283.

(Wöhler). The green salt is found in commerce under the improper name of *distilled verdigris*. The acetates of copper and potash unite in single equivalents, and form a double salt in fine blue crystals, containing 8HO. *Verdigris* is a sub-acetate of copper, formed by placing plates of the metal in contact with the fermenting marc of the grape, or with cloth dipped in vinegar. The bluer species, which consists of minute crystalline plates, is a definite compound of 1 eq. acetic acid, 2 eq. oxide of copper, and 6 eq. of water, $C_4H_3CuO_4.CuO + 6HO$. The ordinary green species is a mixture of the sesqui- and tribasic acetates of copper, with the preceding bibasic acetate. Water dissolves out from verdigris the *sesquibasic acetate*, which presents itself on evaporating the solution, sometimes as an amorphous mass, and sometimes in crystalline grains of a pale blue colour. The sesquibasic acetate consists of 2 eq. of acetic acid, 3 eq. of oxide of copper, and 6 eq. of water; it loses 3 eq. of water at 212°. The *tribasic acetate* is the insoluble residue which remains after the lixiviation of verdigris. It is a clear green powder, which loses nothing at 212°. It contains 2 eq. of acetic acid, 6 eq. oxide of copper, and 3 eq. of water (Berzelius).

Acetate of copper also combines with acetate of lime, and with several other salts. The double *acetate and arsenite of copper* is a crystalline powder of a brilliant sea-green colour, which is used as a pigment, under the name of Schweinfurt green. It is obtained by mixing boiling solutions of equal parts of arsenious acid and neutral acetate of copper, adding to the mixture its own volume of cold water, and leaving the whole at rest for several days. It is a highly poisonous substance. From the analysis of Ehrmann, its formula is $C_4H_3CuO_4 + 3(CuO.AsO_3)$.

The most important *alloys of copper* are those which it forms with tin and zinc:

100 parts of copper with 5 tin (or 4 tin + 1 zinc) form the bronze used for coin.

100 parts copper with 10 tin, form bronze and gun-metal.
100 parts copper with 20 to 25 tin, form bell-metal.
100 parts copper with 30 to 35 tin, form speculum-metal.

A little arsenic is generally added to the last alloy, to increase its whiteness.

The different varieties of brass are prepared, either by fusing together the two metals, copper and zinc, or by heating copper under a mixture of charcoal and calamine—an operation in which zinc is reduced and its vapour absorbed by the copper. Two or three parts of copper to one of zinc form common brass. The brass known as Muntz's white metal, which resists the solvent action of sea-water much better than pure copper, and is, in consequence largely used for the sheathing of ships, consists of 60 parts copper to 40 parts zinc, and appears to be the atomic compound Cu_2Zn. Equal parts of copper and zinc, or four of the former and one of the latter, give an alloy of a higher colour, resembling gold, and on that account called *similor*.

ESTIMATION OF COPPER, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Copper is best precipitated by caustic potash, which when added to a boiling solution of a cupric salt, throws down the protoxide of copper in the form of a heavy black powder. From this precipitate every trace of potash may be removed by washing with hot water; and the washed precipitate may then be dried and ignited in a platinum or porcelain crucible. It must be weighed immediately after cooling, with the cover on the crucible, because it absorbs moisture rapidly from the air. It contains 79·82 per cent. of copper (H. Rose).

Copper is often precipitated from its solutions by hydrosulphuric acid. In that case the precipitated sulphide must be washed as quickly as possible with water containing hydrosulphuric acid, to prevent oxidation; the precipitate may

then be dried, and the filter burnt with the precipitate on it, in a porcelain basin; after which the precipitate is treated with concentrated nitric acid, which dissolves it, with separation of sulphur, and the copper precipitated from the filtered solution by potash as above. The chief precaution to be attended to in this process is to wash the precipitated sulphide quickly, and to preserve it as completely as possible from contact with the air; otherwise the sulphide becomes partially oxidised and converted into sulphate, which being soluble, runs through the filter; when this takes place, the filtrate becomes brown, because the copper thus carried through, is again precipitated by hydrosulphuric acid.

Volumetric methods.—Copper may be volumetrically determined by means of a solution of permanganate of potash, by a process founded on that adopted by Margueritte for the determination of iron (p. 56.). The copper compound having been weighed and dissolved in acid, is mixed in a porcelain basin, with neutral tartrate of potash and excess of caustic potash, and then heated with a quantity of milk-sugar, or honey, sufficient to precipitate all the copper as cuprous oxide, the completion of the precipitation being indicated by the brown colour which the liquid then acquires. The precipitated cuprous oxide is then filtered, washed with hot water, and gently heated, together with the filter, with a mixture of pure sesquichloride of iron and dilute hydrochloric acid. It is thereby dissolved in the form of protochloride of copper, the sesquichloride of iron being at the same time reduced to protochloride:

$$Cu_2O + Fe_2Cl_3 + HCl = 2CuCl + 2FeCl + HO.$$

In the filtered liquid, diluted to a convenient strength and heated to about 86°, the quantity of iron in the state of protochloride is determined by a graduated solution of permanganate of potash in the manner already described (p. 56.), and thence the equivalent quantity of copper is readily determined. The presence of lead, zinc, bismuth, manganese, or iron, in the

alkaline solution does not interfere with the process; silver or mercury must be separated before the precipitation of the cuprous oxide.

Another method, which appears to give very exact results, is to treat the copper-solution with iodide of potassium, whereby diniodide of copper is precipitated and iodine set free:

$$2(CuO.NO_5) + 2KI = Cu_2I + I + 2(KO.NO_5),$$

and remove the free iodine by means of a standard solution of hyposulphite of soda, whereby iodide of sodium and tetrathionate of soda are produced:

$$2(NaO.S_2O_2) + I = NaI + NaO.S_4O_5.$$

The copper-compound, if solid, an alloy for example, is dissolved in nitric acid; carbonate of soda added till a slight precipitate is formed; and this precipitate redissolved in acetic acid (free nitric acid would vitiate the result by decomposing the iodide of potassium). A quantity of iodide of potassium is next added, equal to at least six times the weight of the copper to be determined, and then the standard solution of hyposulphite of soda, in sufficient quantity to remove the greater part of the free iodine, which point will be indicated by the colour of the liquid changing from brown to yellow. Lastly, a clear solution of starch is added, and the addition of the hyposulphite of soda cautiously continued till the blue colour of the iodide of starch is completely destroyed. The solution of hyposulphite of soda is graduated by dissolving a known weight of pure electrotype copper in nitric acid, and proceeding as above. If the copper-compound contains a large quantity of lead or iron, these metals must be removed before commencing the determination, because the yellow colour of the iodide of lead and the red of the acetate of iron might interfere with the result (E. O. Brown).*

* In a paper read before the Chemical Society, Nov 17th, 1856, and to be Published in the 10th volume of the Society's Journal.

Pelouze's method, which consists in treating the copper solution with excess of ammonia, and precipitating the copper as oxysulphide, CuO.5CuS, by adding a graduated solution of sulphide of sodium till the blue colour is completely destroyed, appears, from Mr. Brown's experiments, to be liable to uncertainty from two causes: first, because the oxysulphide of copper reduces a portion of the protoxide of copper to dioxide, thereby rendering the solution colourless before the precipitation is complete; and secondly, because a portion of the sulphide of sodium is oxidised and converted into hyposulphite of soda.

Copper is separated from all the preceding metals, except cadmium, by means of hydrosulphuric acid, the solution being previously acidulated with hydrochloric or sulphuric acid. When zinc, nickel, or cobalt is present, a considerable excess of acid must be added, otherwise a portion of these metals will be precipitated together with the copper.

From *cadmium*, copper may be separated by carbonate of ammonia, which dissolves the copper and leaves the cadmium. The deposition of the cadmium is not complete till the liquid has been exposed for some time to the air. The separation is, however, better effected by adding to the solution of the two metals a quantity of cyanide of potassium, sufficient to redissolve the precipitate first formed, and then passing hydrosulphuric acid through the solution. Sulphide of cadium is then precipitated, and on driving off the excess of hydrosulphuric acid by heat, and adding more cyanide of potassium, the sulphide of copper remains completely dissolved. The copper may be precipitated as sulphide by mixing the filtrate with hydrochloric acid: but it is better to boil the filtrate with aqua-regia, till all the hydrocyanic acid is expelled, and then precipitate the copper by potash (Haidlen and Fresenius).

SECTION VIII.

LEAD.

Eq. 103·56 *or* 1294·5; Pb (*plumbum*).

Lead was one of the earliest known of the metals. A considerable number of its compounds are found in nature, but the sulphide, or galena, is the only one which is important as an ore of lead. The reduction of the metal is effected by heating the sulphide with exposure to air (or roasting), by which much of the sulphur is burned and escapes as sulphurous acid, and a fusible mixture of oxide of lead and sulphate of lead is produced. A fresh portion of the ore is added, which reacts upon the oxide of lead, the sulphur and oxygen forming sulphurous acid, and the lead of both oxide and sulphide being consequently reduced. Lime also is added, which decomposes the sulphate of lead, and exposes the oxide to be reduced by the fuel or by sulphide.

Lead has a bluish grey colour and strong metallic lustre, is very malleable, and so soft, when it has not been cooled rapidly, as to produce a metallic streak upon paper. Its density is 11·445, and is not increased by hammering. Its tenacity is less than that of any other ductile metal. The melting point of lead is 612°; on solidifying, this metal shrinks considerably, so that bullets cast in a mould are never quite round. Lead, like most other metals, assumes the octohedral form on crystallising. Lead is one of the less oxidable metals, at least when massive; its surface soon tarnishes, and is covered with a grey pellicle, which appears to defend the metal from further change. Rain or soft water cannot be preserved with safety in leaden cisterns, owing to the rapid formation of a white hydrated oxide at the line where the metal is exposed

to both air and water; the oxide formed is soluble in pure water, and highly poisonous. But a small quantity of carbonic acid, which spring and well water usually contain, arrests the corrosion of the lead, by converting the oxide of lead into an insoluble salt, and prevents the contamination of the water.* Lead is not directly attacked by hydrochloric and sulphuric acids, at the usual temperature, but they favour its union with oxygen from the air. Its best solvent is nitric acid. Besides a protoxide, PbO, which is a powerful base, lead forms a suboxide Pb_2O, and a bioxide PbO_2, which do not combine with acids.

Suboxide of lead, Pb_2O, was discovered by Dulong, and is best obtained by heating the oxalate of lead to low redness in a small retort. It is dark grey, almost black, and pulverulent, and is not affected by metallic mercury. According to the analysis of Boussingault, it contains 1 eq. of oxygen to 2 eq. of lead. The grey pellicle which forms upon lead exposed to the air is, according to Berzelius, the same suboxide.

Protoxide of lead, PbO, 111·56 *or* 1394·5.—When a stream of air is thrown upon the surface of melted lead, the metal is rapidly converted into the protoxide, of a sulphur-yellow colour. The oxidated skimmings of the metal are, in this condition, termed *massicot*, and were at one time used as a yellow pigment. This preparation is fused at a bright red heat, and the oxide is thus separated from some metallic lead, with which it is intermixed in massicot. The fused oxide, on solidifying, forms a brick-red mass, which divides easily into crystalline scales, tough and not easily pulverised; they form *litharge*. The protoxide of lead can be obtained distinctly crystallised by various processes, but always presents itself in the same form, an octohedron with a rhombic base (Mitscherlich). By igniting the subnitrate of lead, the protoxide is obtained very pure, and of a rich lemon-yellow colour. Its density after fusion is 9·4214.

* Dr. Christison's Treatise on Poisons.

When the acetate, or any other salt of lead, is precipitated by potash, the protoxide falls as a white hydrate, which may be dried at 212° without decomposition. It contains 3¾ per cent. water, and is, therefore, the hydrate $2PbO . HO$ (Mitscherlich). Oxide of lead likewise crystallises anhydrous, from solution, at the usual temperature, when precipitated under such circumstances that it cannot find water to combine with. This oxide dissolves in above 12,000 times its weight of distilled water, which acquires thereby an alkaline reaction, but not in water containing any saline matter. It is soluble in potash or soda; and the solutions, when evaporated, yield small crystals of an alkaline compound. A compound of lime and oxide of lead is obtained in needles, when hydrate of lime and that oxide are heated together, and the solution allowed to evaporate with exclusion of air. This solution has been employed to dye the hair black. Oxide of lead combines readily with the earths and metallic oxides by fusion, and when added to the materials of glass, imparts brilliancy to it and increased fusibility.

Oxide of lead is a powerful base, resembling baryta and strontia, and affords a class of salts which often agree in form and in general properties with the salts of these earths. Its carbonate occurs in *plumbocalcite*, in the form of carbonate of lime, an isomorphism by which the protoxide of lead is connected with the magnesian oxides. All its soluble salts are poisonous, although no salt of lead, with the exception of the insoluble carbonate, is highly so (Dr. A. T. Thomson). In a case of accidental poisoning by the carbonate, acetic acid proved a sufficient antidote.

Caustic alkalies precipitate lead from its solutions as a white hydrate, soluble in potash and soda, insoluble in ammonia. *Alkaline carbonates* throw down a white precipitate of carbonate of lead, insoluble in excess of the reagent. *Hydrochloric acid* and *soluble chlorides* produce in moderately strong lead-solutions, a white crystalline precipitate of chloride

of lead, easily soluble in potash, insoluble in ammonia, soluble in a considerable quantity of water; in dilute solutions (*e. g.* in a solution of 1 part of nitrate of lead in 100 parts of water) no precipitate is formed. *Sulphuric acid* and *soluble sulphates* throw down, even from very dilute solutions, a white, pulverulent precipitate of sulphate of lead, easily soluble in potash, soluble also, though slowly, in hydrochloric and nitric acid; but by adding a considerable excess of sulphuric acid, lead may be completely precipitated even from solutions containing hydrochloric or nitric acid. According to Lassaigne, 1 part of oxide of lead (in the form of nitrate) dissolved in 25,000 parts of water, gives an opalescence with sulphate of soda, after a quarter of an hour. *Hydrosulphuric acid* and *alkaline sulphides* produce a black precipitate of sulphide of lead, insoluble in sulphide of ammonium. In very dilute solutions, only a brown colouring is produced, the limit of the reaction being attained, according to Lassaigne, with 1 part of oxide of lead (in the form of nitrate) dissolved in 350,000 parts of water. If the solution of the lead-salt contains free hydrochloric acid, the precipitate is red or yellow, and a large excess of hydrochloric acid prevents it altogether. *Iodide of potassium* produces a bright yellow precipitate of iodide of lead, which dissolves in boiling water and separates again on cooling in crystalline spangles, exhibiting a beautiful play of colours. *Chromate* and *bichromate of potash* throw down yellow chromate of lead, easily soluble in caustic potash. The limit of this reaction is attained with 1 part of oxide of lead (in the form of nitrate) dissolved in 70,000 parts of water (Harting). *Iron* and *zinc* throw down metallic lead. If a mass of zinc be suspended in a solution, made by dissolving one ounce of acetate of lead in two pounds of distilled water, the lead is precipitated in beautiful crystalline plates, which are deposited not only in metallic contact with the zinc, but extend from it to a considerable distance in the liquid, forming what is called the lead-tree. Lead-salts, mixed with

carbonate of soda or cyanide of potassium, and ignited on charcoal before the blow-pipe, yield a malleable button of lead. The oxides of lead are reduced by simply heating them with the blowpipe flame on charcoal.

Sesquioxide of lead, Pb_2O_3.—Hypochlorite of soda throws down from lead-salts a reddish-yellow mixture of sesquioxide and chloride of lead. The sesquioxide may be obtained free from chloride by supersaturating a solution of nitrate of lead with potash, in quantity sufficient to redissolve the precipitated hydrate, and then treating it with hypochlorite of soda. The sesquioxide is converted by acids into bioxide and an ordinary salt of lead (Winkelblech).

Bioxide or peroxide of lead, PbO_2, may be obtained in the same manner as the peroxides of cobalt and nickel, by exposing the protoxide suspended in water to a stream of chlorine; also by fusing protoxide of lead with chlorate of potash at a temperature short of redness; or by digesting the following intermediate oxide, minium, in diluted nitric acid, which dissolves the protoxide of lead, decanting off the nitrate of lead, and washing the powder which remains with boiling water. Wöhler precipitates a solution of 4 parts of acetate of lead with a solution of 3 parts or rather more of crystallised carbonate of soda, and passes chlorine gas through the resulting thin pulpy mass, till the whole of the carbonate of lead is converted into brown bioxide, amounting to 2½ parts, which may then be washed. No chloride of lead is formed in this reaction, the whole of the chlorine combining with the sodium, while acetic and carbonic acid are set free. Bioxide of lead is of a dark earthy-brown colour. It loses half its oxygen by ignition; absorbs sulphurous acid with great avidity, and becomes sulphate of lead; and affords chlorine when digested in hydrochloric acid.

Minium or red lead is formed by heating massicot or protoxide of lead, which has not been fused, to incipient redness in a flat furnace, of a particular construction, and directing a

current of air upon its surface. Oxygen is absorbed, and an oxide formed of a fine red colour, with a shade of yellow. It is not constant in composition. The proportion of oxygen, when the absorption is least considerable, approaches that of a compound containing $3PbO.PbO_2$; and such was the composition of a crystallised compound of a fine red colour, formed by accident in a minium furnace, and analysed by Houton-Labillardière. But when the absorption is favoured by time and most considerable, it approaches but never exceeds 2·4 per cent. of the original weight of the protoxide. This result agrees with the formula Pb_3O_4, and accordingly minium may be regarded as a compound of protoxide and bioxide of lead $2PbO.PbO_2$, or of protoxide and sesquioxide $PbO.Pb_2O_3$. A sample of minium analysed by Longchamps contained $5PbO.PbO_2$. The finest minium is obtained by calcining oxide of lead from the carbonate, at about 600°.

Minium is not altered by being heated in a solution of acetate of lead, which is capable of dissolving free protoxide of lead. When heated to redness, it loses oxygen, and leaves the protoxide. It does not combine with acids, but is resolved by a strong acid into bioxide of lead and protoxide, the latter combining with the acid. When minium is treated with concentrated acetic acid, it first becomes white, and then dissolves entirely in a new quantity of acid without colouring it. But the solution gradually decomposes, and bioxide of lead separates from it of a blackish-brown colour (Berzelius).

Protosulphide of lead, PbS, is thrown down from salts of lead, by hydrosulphuric acid, as a black precipitate, which is insoluble in diluted acids or in alkalies. It forms also the ore galena, which crystallises in the cube and other forms of the regular system; its density is 7·585. Sulphide of lead is decomposed easily by nitric acid, and converted into nitrate and sulphate of lead, with separation of a little sulphur. The more concentrated the nitric acid, the greater is the quantity of sulphate produced. Recently precipitated sulphide of lead

may be completely dissolved in the form of nitrate by boiling with dilute nitric acid. Concentrated and boiling hydrochloric acid dissolves sulphide of lead, with disengagement of hydrosulphuric acid gas. Galena may be united by fusion with more lead, and gives the subsulphides Pb_4S, and Pb_2S. When a solution of persulphide of potassium is added to a salt of lead, a blood-red precipitate appears, which is a persulphide of lead, but is almost immediately changed into the black protosulphide of lead and free sulphur.

Chloride of lead, PbCl, 139·06 *or* 1738·25.—Lead dissolves slowly in hydrochloric acid, by substitution for hydrogen, forming the chloride of lead, but only when assisted by the action of the air. The same compound is obtained by digesting oxide of lead in hydrochloric acid, and also falls as a white precipitate, when a salt of lead is added to any soluble chloride. The chloride of lead is soluble in 135 times its weight of cold water, and more so in hot water, from which it crystallises on cooling in long flattened acicular crystals, which are anhydrous. It is very fusible, and may be sublimed at a higher temperature

Oxychloride of lead.—Chloride of lead combines in five different proportions with the protoxide, forming the following compounds:—*a.* 3PbCl.PbO. Four parts of chloride of lead ignited with 1 part of litharge yield a fused, laminar, pearl-grey mixture, which, when triturated with water, swells up to a bulky mass having the above composition (Vauquelin). The same substance is obtained by Mr. Pattinson, by decomposing carbonate of lead with lime-water, and used as a white pigment.—*b.* PbCl.PbO. Formed by igniting chloride of lead in contact with air till it no longer fumes, or by fusing chloride and carbonate of lead together. Carbonic acid is then set free, and a compound formed which is of a deep yellow colour while fused, but as it cools assumes a lemon-yellow colour, and becomes nacreous and crystalline (Döbereiner).—*c.* PbCl.2PbO. This compound forms the mineral *Mendipite*,

found at Mendip, in Somersetshire, where it occurs in yellowish-white, right rhombic prisms, which are harder than gypsum, translucent, and have an adamantine lustre (Berzelius). It also occurs, and in a state of greater purity, at Brilon, near Stadtbergen, in Westphalia; the crystals there found are white, translucent, and have a mother-of-pearl lustre on the cleavage surfaces.* — *d.* PbCl.3PbO. Obtained by fusing 1 eq. chloride of lead with 3 eq. of the protoxide; also in the hydrated state, PbCl.3PbO + HO or 4PbO.HCl, by decomposing chloride of lead with ammonia; by precipitating subacetate of lead with common salt; and by decomposing a solution of common salt with protoxide of lead. The hydrate is a white flocculent mass, and when fused yields the anhydrous compound, which is a greenish-yellow laminated mass, forming a yellow powder. — *e.* PbCl.5PbO. Obtained by fusing 1 eq. chloride of lead with 5 eq. of the protoxide. Orange-yellow substance, yielding a deep yellow powder. — *f.* PbCl.7PbO, is produced on fusing by heat a mixture of 10 parts of pure oxide of lead and 1 part of pure sal-ammoniac, a portion of the lead being at the same time reduced. The surbasic chloride when fused affords cubic crystals on cooling slowly. It forms in that state a beautiful yellow pigment, known as Turner's yellow in this country, and Cassel yellow in Germany. It was prepared in England by digesting litharge with half its weight of common salt, a portion of which is converted into caustic soda, and afterwards washing and fusing the oxychloride formed. But it is sufficient to use 1 part of salt to 7 parts of oxide of lead in this decomposition.

Bichloride of lead, $PbCl_2$.—Bioxide of lead dissolves, without evolution of gas, in cold dilute hydrochloric acid, forming a rose-coloured liquid, from which alkalies throw down the bioxide in its original state. The rose-coloured acid solution, evaporated in vacuo over strong potash-ley, yields crystals

* Rhodius, Ann. Ch. Pharm. lxii. 373.

of chloride of lead PbCl, togther with crystals of a different character, which appear to consist of $PbCl_2$ (Rivot, Beudant, and Daguin).

Bromide of lead, PbBr, is much less soluble in water than the chloride; hence, in a liquid containing hydrochloric and hydrobromic acids, if the bromine be precipitated by acetate of lead, the filtered liquid will still contain chlorine, which may then be detected by adding nitrate of silver (H. Rose).

Iodide of lead, PbI, 229·92 *or* 2874.—Appears as a beautiful lemon-yellow powder, when iodide of potassium is added to a salt of lead. It is soluble in 194 parts of boiling water, and in 1235 parts of water at the usual temperature, and may be obtained from solution in brilliant hexagonal scales of a golden-yellow colour. A compound of a paler yellow, which appears in dilute solutions and when the salt of lead is in excess, is a basic iodide. M. Denot finds three oxy-iodides of lead, containing 1 eq. of iodide of lead to 1 eq., 2 eq., and 5 eq. of oxide of lead, and always 1 eq. of water, which last they do not lose below a temperature of about 400°.

Neutral iodide of lead, PbI, is decomposed by metallic chlorides, yielding, when the iodide is in excess, compounds which may be regarded as iodide of lead, in which part of the iodine is replaced by chlorine. Sesquichloride of iron and protochloride of copper separate free iodine (A. Engelhardt).

Cyanide of lead, PbCy, is a white insoluble powder, obtained by precipitation.

Carbonate of lead, ceruse, white lead; $PbO.CO_2$; 133·56 *or* 1669·5.—Occurs in nature well crystallised, in the form of carbonate of baryta. It is precipitated as a white powder, of which the grains, although very minute, are crystalline, when an alkaline carbonate is added to the acetate or nitrate of lead. The precipitate is anhydrous. When oxide of lead is left covered with water in an open vessel, it absorbs carbonic acid, and becomes white, forming the subcarbonate $PbO.CO_2 + PbO.HO$.

Carbonate of lead is invaluable as a white pigment, from its great opacity, which gives it that property called *body* by painters, and enables it to cover well. As precipitated by an alkaline carbonate, it is deficient in body, owing to the transparency of the crystalline grains composing the precipitate. It is also a neutral carbonate, as thus prepared, and differs in composition from the ceruse of commerce, which Mulder finds always to contain hydrated oxide of lead in combination with the carbonate of lead. The result of Mulder's analyses of numerous specimens of white lead, is, that there are three varieties of that substance, the composition of which is expressed by the three following formulæ:—

$$2(PbO.CO_2)+PbO.HO;$$
$$5(PbO.CO_2)+3(PbO.HO);\text{ and}$$
$$3(PbO.CO_2)+PbO.HO.$$

Mr. J. A. Phillips has also examined several specimens of white lead prepared by the Dutch process. Four samples gave by analysis the formula, $2(PbO.CO_2)+PbO.HO$; one gave $3(PbO.CO_2)+PbO.HO$; another, $5(PbO.CO_2)+PbO.HO$.* Dr. T. Richardson also found that varieties of white lead contain a portion of oxide of lead, in addition to the carbonate, and so far confirms the conclusions of Mulder.

In the old or Dutch mode of preparing white lead, which is still extensively practised, thin sheets of the metal are placed over gallipots containing weak acetic acid (water with about 2½ per cent. dry acid), themselves imbedded in fermenting tan, the temperature of which varies from 140° to 150°. The action is often very rapid, and the metal disappears in a few weeks to the centre of the sheet. In this process, from 2 to 2½ tons of lead (4480 to 5600 pounds) are converted into carbonate, by a quantity of vinegar which does not contain more than the small quantity of 50 pounds of dry acetic acid. Hence the metal is certainly neither oxidised nor carbonated in this process, at the expense of the acetic acid. The oxygen

* Chem. Soc. Qu. Pt. iv. p. 165.

must be derived from the air, and the carbonic acid from the fermenting tan. In the newer process, litharge, without any preparation, is mixed with water and about 1 per cent. of acetate of lead, and carbonic acid gas passed over it; the oxide of lead is rapidly converted into excellent ceruse. There can be little doubt that all the oxide of lead is successively dissolved by the acetate, and presented to the carbonic acid as a soluble subacetate; a compound which, it is known, absorbs carbonic acid with the greatest avidity, and allows its excess of oxide to precipitate as carbonate of lead. The new process supplies likewise the theory of the old one, the function of the acetic acid being manifestly the same in both processes. Nitrate of lead has been substituted for the acetate, with other things the same as in the last process.

Sulphate of lead; PbO, SO_3; 151·56 *or* 1894·5.—This salt is precipitated when sulphuric acid or a soluble sulphate is added to a solution of acetate or nitrate of lead, as a white, dense, insoluble precipitate, which appears by the microscope to be composed of minute crystals. It is also formed by the action of strong nitric acid on sulphide of lead. Sulphate of lead contains in 100 parts, 26·44 sulphuric acid and 73·56 oxide of lead, and may be exposed to a red heat without decomposition. Dr. Richardson finds that this salt acquires considerable opacity, and may be substituted for ceruse, when prepared in a mode analogous to the new process for that substance; namely, by supplying sulphuric acid, in a gradual manner, to a thick mixture of litharge and water containing a small proportion of acetate of lead. In this manner the sulphate of lead may be obtained united with any desirable excess of oxide of lead.

Nitrate of lead; $PbO.NO_5$; 165·56 *or* 2069·5.— Obtained by dissolving litharge, at the boiling point, in slightly diluted nitric acid, which should be free from hydrochloric and sulphuric acids. The neutral nitrate crystallises in large octohedrons, with the secondary faces of the cube, sometimes

transparent, although generally white and opaque. The crystals are anhydrous; they are soluble in $7\frac{1}{2}$ times their weight of cold, and in a much smaller quantity of hot water. Nitrate of lead is decomposed by an incipient red heat, yielding a mixture of oxygen gas and peroxide of nitrogen (which is prepared in this way), and leaving the yellow oxide of lead. When a small quantity of ammonia is added to nitrate of lead, or when a dilute solution of the neutral salt is boiled with oxide of lead in fine powder, a soluble *bibasic nitrate of lead* is formed $PbO.NO_5 + PbO$. It crystallises during evaporation in fine scales, or in little opaque grains, which are anhydrous. The granular crystals decrepitate when heated, with extraordinary force. The *tribasic nitrate of lead* precipitates when ammonia is added in very slight excess to a solution of nitrate of lead. Its constituents are $2(3PbO.NO_5) + 3HO$ (Berzelius). It is a white powder, which is soluble to a small extent in pure water. When nitrate of lead is digested with a considerable excess of ammonia, the decomposition stops at the point at which 6 eq. of oxide of lead are combined with 1 eq. of nitric acid. The *sexbasic nitrate of lead* contains $2(6PbO.NO_5) + 3HO$ (Berzelius).

Nitrites of lead. — When a solution of 100 parts of nitrate of lead is boiled with 78 parts of metallic lead in thin turnings, the lead is dissolved, and a little nitric oxide is evolved, in consequence of a partial decomposition of nitrous acid previously formed. The solution is alkaline and yellow; and gives, on cooling, brilliant crystalline plates of a golden yellow colour, which consist of the *bibasic nitrite of lead*, $2PbO.NO_3$. By dissolving 100 parts of this salt in water at 167° (75° C.), and then mixing with the solution 35 parts of oil of vitriol, previously diluted with four times its weight of water, one half of the oxide of lead is precipitated as sulphate of lead, and a solution is obtained of a deep yellow colour, from which the *neutral nitrite of lead*, $PbO.NO_3 + HO$, crystallises. This salt gives yellow crystals, resembling the nitrate in form. Its

solution absorbs oxygen from the air, and, like all the nitrites, gives off nitric oxide at 176° (80° C.), while a subnitrite of lead precipitates. Berzelius, to whom we are indebted for the preceding facts, also formed a *quadribasic nitrite of lead*, containing $NO_3.4PbO + HO$, by boiling 1 part of nitrate of lead, and 1½ parts or more of metallic lead, in a long-necked flask for 12 hours, then filtering and leaving the solution to crystallise by cooling: it thus yields pale, flesh-coloured, silky needles, or, if rapidly cooled, a white powder.

The nitrites of lead have also been examined by other chemists, who have obtained results differing from those of Berzelius. Thus, Péligot and others found that Berzelius's bibasic nitrite contains the elements of 2 eq. of oxide of lead, 1 eq. of hyponitric acid, NO_4, and 1 eq. of water. Gerhardt therefore regards it as a compound of bibasic nitrate and bibasic nitrite of lead:—

$$2(PbO.NO_4) = 2PbO.NO_3 + 2PbO.NO_5.$$

and expresses its formation by the equation:—

$$2(PbO.NO_5) + 2Pb = 2PbO.NO_5 + 2PbO.NO_3.$$

If the action of the metallic lead be further continued, a fresh portion of nitrate is deoxidised, and the result is an orange-coloured salt, containing $7PbO.2NO_4$ (Péligot), which Gerhardt regards as a double salt more basic than the former:

$$7PbO.2NO_4 = 4PbO.NO_3 + 3PbO.NO_5.$$

Finally, by the continued action of the lead, the subnitrate contained in these two salts is likewise reduced, and a subnitrite is formed, viz., either Berzelius's quadrobasic salt, $4PbO.NO_3$, or a bibasic nitrite $2PbO.NO_3$, obtained by Bromeis. The last salt crystallises in long golden-yellow needles containing 1 eq. of water.*

Phosphate of lead.—On mixing nitrate of lead with ordi-

* For a more detailed account of the nitrates and nitrites of lead, see Gmelin's Handbook, Translation, v. 152—157.

nary phosphate of soda, a precipitate is formed containing the two salts $3PbO.PO_5$ and $2PbO.HO.PO_5$. The latter is obtained pure by precipitating a boiling solution of nitrate of lead with pure phosphoric acid. This salt dissolves in nitric acid and fixed alkalies, but very sparingly in acetic acid; ammonia converts it into $3PbO.PO_5$. It fuses readily before the blowpipe, and crystallises on cooling in well defined polyhedrons. When strongly ignited with charcoal, it gives off phosphorus and carbonic oxide, and leaves metallic lead.

Chlorite of lead, $PbO.ClO_3$, is obtained in sulphur-yellow crystalline scales by precipitating nitrate of lead with an excess of chlorite of baryta containing free chlorous acid. It decomposes at 259° with a kind of explosion, and sets fire to flowers of sulphur triturated with it. Sulphuric acid diluted with an equal weight of water, decomposes it, especially between 104° and 122°, evolving pure chlorous acid gas, and leaving 88·75 per cent. of sulphate of lead (Millon).

Chlorate of lead, $PbO.ClO_5 + HO$, is obtained by cooling a hot solution of oxide of lead in aqueous chloric acid, in rhomboïdal prisms belonging to the oblique prismatic system, and isomorphous with the analogously constituted crystals of chlorate of baryta. These crystals, when heated, leave the yellow oxychloride $PbO.2PbCl$ (Vauquelin, Wächter, Vogel).

Perchlorate of lead, $PbO.ClO_7$.—The solution of oxide of lead in warm aqueous perchloric acid, yields small prisms having a sweet but highly astringent taste, soluble in their own weight of water, but not deliquescent (Serullas). By boiling a concentrated solution of this salt with carbonate of lead, a solution of a basic salt is obtained, which if the excess of base is very large, yields by evaporation, dull, indistinct crystals, which are resolved by water into a solution of bibasic salt, and a white insoluble residue. When the excess of base is less, or when the solution of the bibasic salt is left to evaporate, crystals of two different forms are obtained; both, however, containing $2PbO.ClO_7 + 2HO$ (Marignac).

Chlorophosphate of lead, $PbCl+3(3PbO.PO_5)$, occurs as *pyromorphite* and *green* and *brown lead-ore.* The crystals belong to the hexagonal system, and have the hardness of apatite. It fuses readily, and on cooling solidifies with vivid incandescence into an angular crystalline mass. In some of these ores, the chloride of lead is partly replaced by fluoride of calcium, and the triphosphate of lead by the triphosphate of calcium or trisarseniate of lead. The calcareous ores may be regarded as mixtures of apatite and pyromorphite. The same compound containing, however, an atom of water, is formed artificially on pouring a boiling solution of chloride of lead into a boiling solution of phosphate of soda, the latter being in excess (Heintz). When, on the contrary, a boiling solution of phosphate of soda is poured into an excess of chloride of lead, a precipitate is formed, which, according to Heintz, is $2(3PbO.PO_5)+PbCl$, but, according to Gerhardt, $2PbO.HO.PO_5+PbCl$.

Acetate of lead, $PbO.(C_4H_3O_3)+3HO$.—This salt is met with well crystallised, and in a state of great purity, in commerce. It is generally prepared by dissolving litharge in the acetic acid procured by the distillation of wood. It crystallises in flattened four-sided prisms; has a taste which is first sweet and then astringent; is very soluble in water, 100 parts of water dissolving 59 of the salt at 60°; and dissolves in 8 parts of alcohol. It effloresces in air, and is apt to be partially decomposed by the carbonic acid of the air, and thus to become partially insoluble. It loses the whole of its water when dried at the usual temperature in vacuo. M. Payen crystallised the anhydrous acetate from solution in absolute alcohol.

Tribasic subacetate of lead, $PbO.(C_4H_3O_3)+2PbO$, is formed by digesting oxide of lead in a solution of the neutral salt, till it is strongly alkaline. This salt does not crystallise when so prepared, but may be dried, and then contains no water. It is very soluble, but must be dissolved in distilled water, as the carbonic, hydrochloric and other acids in well water precipi-

tate its oxide of lead. M. Payen has observed that the tribasic subacetate crystallises readily, in fine prismatic needles, when formed by adding ammonia to a moderately strong solution of the neutral acetate. The crystals contain 1 eq. of water, which they lose at 212°. The acetate of ammonia, formed at the same time, appears to give stability to the subacetate of lead in solution, and prevents an excess of a whole equivalent of ammonia from throwing down any oxide of lead from the solution. This ammoniacal solution of the subacetate of lead, prepared without an excess of ammonia, is a convenient form in which to apply that salt as a reagent.*

Sesquibasic acetate of lead, $3PbO.2(C_4H_3O_3)+HO$.—This salt was obtained by Payen by adding 1 eq. of the neutral acetate to a concentrated and boiling solution of 1 eq. of the tribasic acetate. It is also produced when the neutral and anhydrous acetate of lead is heated in a retort or porcelain capsule, till the whole, after being liquid, becomes a white and porous mass. The sesquibasic acetate is then formed by the decomposition of 3 eq. of neutral acetate of lead, from which there separate the elements of 1 eq. of acetic acid, in the form of carbonic acid and acetone (Matteucci and Wöhler). This basic salt is very soluble, and crystallises in plates of a pearly lustre. Another method of obtaining it is to digest an aqueous solution of 2 eq. of the neutral acetate with 1 eq. of protoxide of lead free from carbonate, till it dissolves, and evaporate the filtrate in vacuo over oil of vitriol.

A *sexbasic acetate of lead*, $6PbO.(C_4H_3O_3)$, is formed on dropping a solution of the neutral, or of tribasic acetate of lead, into excess of ammonia. It is a white precipitate, which when examined by the microscope, has a crystalline aspect. It contains a little water, which it loses when dried in vacuo.

A *bibasic acetate*, $2PbO.(C_4H_3O_3)$, is also formed, accord-

* Mémoire sur les Acétates et le Protoxide de Plomb, par M. Payen, An. de Chim. et de Phys. t. lxvi. p. 37.

ing to Döbereiner and Schindler, by boiling 1 eq. of neutral acetate of lead with 1 eq. of the protoxide.

The common *extractum Saturni* of the pharmacopœias appears to consist chiefly of bibasic acetate, containing more or less of the tribasic and sesquibasic salts.

Alloys of lead.—Lead and tin may be fused together in all proportions. M. Rudberg finds that these metals combine in certain definite proportions, having fixed points of congelation:—

1 atom of lead and 3 atoms of tin, congeal at 368·6°.
1 atom of lead and 1 atom of tin, at 464°.
2 atoms of lead and 1 atom of tin, at 518°.
3 atoms of lead and 1 atom of tin, at 536°.

A thermometer placed in a fluid alloy of 1 atom of lead and 2 atoms of tin, becomes stationary when the temperature falls to 392°; a portion then solidifies, and a more fusible alloy separates; the temperature again falls, and afterwards becomes stationary at 368·6°, the crystallising point of the alloy composed of 1 atom of lead and 3 atoms of tin. If the alloy contains so much tin that its point of complete congelation is below 368·6°, the last compound always separates from it at that point, and the thermometer remains stationary for a time, whatever may be the proportion of the metals in the alloy.* *Fine solder* is an alloy of 2 parts of tin and 1 of lead; it fuses at about 560°, and is much employed in tinning copper. *Coarse solder* contains one fourth of tin, and fuses at about 500°; it is the substance employed for soldering by plumbers.

Lead, as reduced from the native sulphide, always contains a little silver. The latter is separated by allowing two or three tons of the melted metal to cool slowly in a hemispherical iron pot, when the lead, as it solidifies, separates in crystals, which can be raked out. The silver remains almost wholly in the

* Rudberg, An. Ch. Phys. [2.] xlviii. 363.

more fusible portion, or what may be looked upon as the mother-liquor of these crystals; so that by this operation the argentiferous alloy is greatly concentrated. This mode of separation was discovered by Mr. Pattinson of Newcastle. To separate the remaining lead, much of it is converted into massicot, by the action of air upon its surface, in the shallow furnace used for that preparation; and the last portions of lead are removed by continuing the oxidation upon a porous bason or *cupel* of bone-earth, which imbibes the fused oxide of lead, while the melted silver is found in a state of purity upon the surface of the cupel, not being oxidable at a high temperature.

ESTIMATION OF LEAD, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Lead may be estimated either as protoxide or as sulphate. For the former mode of estimation, it is best to precipitate by oxalate of ammonia, the solution being neutral or rendered very slightly alkaline by ammonia. The oxalate of lead, after being washed and dried, is then to be ignited in an open porcelain crucible, whereby it is converted into protoxide. As lead is very easily reduced by carbonaceous matter at a red heat, the precipitate must not be ignited in contact with the filter; but the filter, after the greater part of the precipitate has been removed from it, must be held on the point of a fine platinum wire above the crucible, and set on fire, so that the ashes may drop in; the precipitate may then be added, and the ignition completed. The protoxide contains 92·83 per cent. of metallic lead. Lead may also be precipitated by carbonate of ammonia, to which a little free ammonia has been added, and the carbonate of lead treated as above.

In precipitating lead as sulphate, if the solution be neutral, the precipitation is best effected by sulphate of soda; the sul-

phate of lead may then be washed on a filter, dried and ignited; but if the solution contains free nitric acid, it is best to precipitate by excess of sulphuric acid, then evaporate to dryness, and ignite till all excess of acid is driven off; treat the residue with water to dissolve out any soluble salts that may be present; wash the sulphate of lead on a filter, and then dry and ignite it, burning the filter separately as above. The sulphate contains 68·32 per cent. of lead.

From the *alkalies* and *earths*, and from *manganese*, *iron*, *cobalt*, *nickel*, and *zinc*, lead is easily separated by hydrosulphuric acid, the solution being previously acidulated with nitric acid. The precipitated sulphide is washed and dried, then placed, together with the filter (which should be as small as possible), in a porcelain dish, covered over with a glass plate or a funnel, and treated with fuming nitric acid, added cautiously and by small portions at a time. Violent action takes place, and the sulphide of lead is converted into sulphate. A portion may, however, be converted into nitrate, with separation of sulphur: hence, to insure complete conversion into sulphate, it is necessary to add a few drops of strong sulphuric acid. The product must then be strongly ignited to drive off the excess of sulphuric acid, and burn away the remaining organic matter of the filter.

From *cadmium* and *copper*, lead is easily separated by sulphuric acid.

ORDER V.

OTHER METALS PROPER HAVING ISOMORPHOUS RELATIONS WITH THE MAGNESIAN FAMILY.

SECTION I.

TIN.

Eq. 58·82 *or* 735·25; Sn (*stannum*).

Tin does not occur native, but its common ore is reduced by a simple process, and mankind appear to have been in possession of this metal from the earliest ages. The most productive mines of tin are those of Cornwall, from which the ancients appear to have derived their principal supply of this metal, and those of the peninsula of Malacca and island of Banca in India.

The only important ore of tin is the bioxide, which is found in Cornwall, both in veins traversing the primary rocks, and in alluvial deposits in their neighbourhood. In the latter case, the ore presents itself in rounded grains of greater or less size, which form together a bed covered by clay and gravel. This ore has evidently been removed from its original situation, and the grains rounded by the action of water, which has at the same time divested it of the other metallic ores with which it is accompanied in the vein; these being softer are more easily reduced to powder, and have been carried away by the stream. This ore, called *stream tin,* is easily reduced by coal, and gives the purest tin. The metal from the ore of the veins is contaminated with iron, copper, arsenic, and antimony, from which a portion of it is partially purified by *liquation.* Bars of the impure metal are

exposed to a moderate heat, by which the pure tin is first melted, and separates it from a less fusible alloy containing the foreign metals. The purer portion is called *grain tin*, and the other, *ordinary tin* or *block tin*. The mass of grain tin is heated till it becomes brittle, and then let fall from a height. By this it splits into irregular prisms, somewhat resembling basaltic columns. This splitting is a mark of the purity of the tin, for it does not happen when the tin is contaminated by other metals.

Pure tin is white, with a bluish tinge, very soft, and so malleable, that it may be beaten into thin leaves, tinfoil not being more than 1-1000th of an inch in thickness. When a bar of tin is bent, it emits a grating sound, which is characteristic; and when bent backwards and forwards rapidly, several times in succession, becomes so hot that it cannot be held in the hand. At the temperature of boiling water, tin can be drawn out into wire, which is very soft and flexible, but deficient in tenacity. The density of pure tin is 7·285, or 7·293 after being laminated; that of the tin of commerce is said to vary from 7·56 to 7·6. Its point of fusion is 442°, according to Crichton and Rudberg; 4456°, according to Kupffer. Tin is volatile at a very high temperature. The brilliancy of the surface of tin is but slowly impaired by exposure to air, and even in water it is scarcely acted upon. Hence the great value of this metal for culinary vessels, and for covering the more oxidable metals, such as iron and copper, when employed as such. Three oxides of tin are known, the protoxide SnO, sesquioxide Sn_2O_3, and bioxide SnO_2.

Protoxide of tin, Stannous oxide; SnO, 66·82 *or* 835·25. Tin dissolves in undiluted hydrochloric acid, at the boiling temperature, by substitution for hydrogen, and forms the protochloride of tin. From this the protoxide is precipitated by an alkaline carbonate, as a white hydrate, which may be washed with tepid water and dried at a temperature not exceeding 176°. It does not contain a trace of carbonic acid.

This white powder dried more strongly in a retort filled with carbonic acid, and heated to redness, gives the anhydrous oxide as a black powder, the density of which is 6·666. In this state, the oxide is permanent; but if a body at a red heat is brought in contact with it in open air, it takes fire and burns, and is entirely converted into bioxide. If hydrated stannous oxide be boiled with a quantity of potash not sufficient to dissolve it entirely, the undissolved portion is converted into small, hard, shining, black crystals of anhydrous stannous oxide, which, when heated to 392°, decrepitate, swell up, fall to pieces, and are converted into an olive-green powder, consisting also of the anhydrous protoxide. Again, on evaporating a very dilute solution of sal-ammoniac, in which hydrated stannous oxide is diffused, that compound is converted, as soon as the sal-ammoniac crystallises, into anhydrous stannous oxide, having the form of a cinnabar-coloured powder. There are, therefore, three modifications of stannous oxide, black, olive-green, and red (Fremy). The red modification is also obtained by digesting thoroughly washed hydrated stannous oxide at a temperature of 133°, in a slightly acid solution of stannous acetate, having a density of 1·06 (Roth).

Protoxide of tin dissolves in acids, and with more facility when hydrated than after being ignited. This oxide is also dissolved by potash and soda, but the solution after a time undergoes decomposition; metallic tin is deposited, and the bioxide is found in solution. The solution of a stannous salt, and of a stannic salt also, is apt to undergo decomposition, when largely diluted with water, and to deposit a subsalt. Stannous salts absorb oxygen from the air, and have a great affinity for that element; they convert the sesquioxide of iron into protoxide, and throw down mercury, silver and platinum in the metallic state from their solutions. *Chloride of gold* produces a purple precipitate in a stannous salt, consisting, it is believed, of the bioxide of

tin in combination with protoxide of gold, a test by which the protoxide of tin may always be distinguished. *Hydrosulphuric acid* produces in neutral or acid solutions of stannous salts, a brown-black precipitate of protosulphide of tin, which, when gently heated with a considerable quantity of sulphide of ammonium containing excess of sulphur, is converted into the bisulphide and dissolved; acids added in excess to this solution precipitate the yellow bisulphide. *Caustic alkalies* and *alkaline carbonates*, added to stannous salts, throw down a white precipitate of hydrated stannous oxide, soluble in caustic potash or soda, but not in ammonia. *Ferrocyanide of potassium* produces a white precipitate, soluble in hydrochloric acid.

Protosulphide of tin, SnS, is formed when sulphur is mixed with tin heated above its melting point; it is also obtained in small dark grey crystalline laminæ, of sp. gr. 4·973, by adding the hydrated sulphide precipitated from a stannous salt by hydrosulphuric acid, to anhydrous protochloride of tin in the melted state, and removing the excess of the protochloride with dilute hydrochloric acid. It is decomposed by dilute hydrochloric acid, with evolution of hydrosulphuric acid.

Protochloride of tin, Salt of tin; SnCl.—This salt may be obtained in the anhydrous state by gradually heating a mixture of equal weights of calomel and tin, and finally distilling the protochloride at a strong red heat. The fused mass on cooling forms a grey solid, of considerable lustre, and having a vitreous fracture. The hydrated chloride, known in commerce as salt of tin, is procured by evaporating the solution of tin in concentrated hydrochloric acid to the point of crystallisation. It is thus obtained in needles, or in larger four-sided prismatic crystals containing 2 eq. of water. They fuse between 100° and 105°. The specific gravity of the crystals is 2·710 at 60°; that of the fused mass at 100°, is 2·588 (Penny). The salt parts with the greater portion, if not the whole of its water at 212°, but if distilled

at a higher temperature, loses hydrochloric acid also, and leaves an oxychloride of tin. It dissolves completely in a small quantity of water; but when treated with a large quantity, is partly decomposed, hydrochloric acid being dissolved, and a light milk-white powder separating, which is a basic chloride, or oxychloride, $SnCl.SnO + 2HO$. Both the crystals and the solution absorb oxygen from the air, and then a basic salt of the sesquioxide is formed which is also insoluble in water. From both these causes, a complete and clear solution of the salt of tin is rarely obtained, unless the water is previously acidulated with hydrochloric acid. This salt is entirely soluble in caustic alkali, but the solution is liable to an ulterior change already mentioned. One part of crystallised protochloride of tin dissolved, together with 3 parts of tartaric acid, in a sufficient quantity of hot water, and carefully neutralised with potash, forms a clear solution, which may be boiled and mixed with any quantity of water without becoming turbid: the white precipitate which forms in it on the addition of a little more potash, especially on heating, is redissolved by a larger quantity of potash (R. Schneider).

When protochloride of tin is heated with a mixture of hydrochloric and sulphurous acids, a yellow precipitate of bisulphide of tin is formed: $6SnCl + 2SO_2 + 4HCl = SnS_2 + 5SnCl_2 + 4HO$. This reaction serves as a test for sulphurous acid.

The protochloride of tin is used in calico-printing, not only as a mordant, but also as a deoxidising agent, particularly to deoxidise indigo, and to reduce to a lower state of oxidation and discharge the sesquioxides of iron and manganese fixed upon cloth.

Protochloride of tin and potassium; $SnCl.KCl$.—Protochloride of tin forms a double salt with chloride of potassium, and also with chloride of ammonium, which compounds crystallise in the anhydrous state, and also with 3 eq. of water, or, according to Rammelsberg, with only 1 equivalent.

Anhydrous protochloride of tin fused in ammoniacal gas, absorbs half an equivalent of that gas, according to Persoz, forming $2SnCl.NH_3$, or rather perhaps $SnCl.(NH_3Sn)Cl$.

Protiodide of tin, SnI, is formed by heating a mixture of granulated tin and iodine. It is obtained in beautiful shining yellowish red prisms by gently boiling concentrated hydriodic acid with strips of tinfoil in a long glass tube for a day, or more readily by heating the acid with the tin in a sealed glass tube to a temperature of 248°, or at most 302° for an hour; after cooling, the remaining portion of tin is found to be covered with crystals. When tinfoil and iodide of amyl were heated together in a sealed tube for a day to 356°, the tinfoil became covered with yellowish-red quadratic octohedrons at the part where the tube cooled most quickly; but at the part which was immersed in the oil-bath, and therefore cooled more slowly, the metal was covered with sulphur-yellow prisms, which became yellowish-red when taken out (Wöhler). Stannous iodide was found by Boullay, jun., to form double salts with other iodides, particularly with the iodides of the alkaline and earthy metals, in which two atoms of the stannous iodide are combined with one of the other iodide.

Carbonic acid does not combine with either of the oxides of tin.

Protosulphate of tin, $SnO.SO_3$.—Tin dissolves in sulphuric acid, concentrated or a little diluted, yielding a saline mass, which forms a brown solution in water and deposits small crystalline needles on cooling.

Protonitrate of tin, $SnO.NO_5$, is obtained by dissolving hydrated protoxide of tin in nitric acid; the solution cannot be concentrated and is easily altered.

Tartrate of potash and tin, $KO.SnO.(C_8H_4O_{10})$ *or* $C_8H_4(KSn)O_{12}$.—Bitartrate of potash dissolves protoxide of tin, and forms a very soluble salt of potash and tin, which, like most of the tartrates, is not precipitated either by caustic alkalies or by alkaline carbonates. An addition of bitartrate

of potash is occasionally made to the solution of tin used in dyeing.

Sesquioxide of tin, Sn_2O_3.—Was obtained by M. Fuchs, by diffusing recently precipitated sesquioxide of iron in a solution of protochloride of tin containing no excess of acid, and afterwards boiling the mixture. A double decomposition occurs, in which sesquioxide of tin precipitates, and protochloride of iron is retained in solution:

$$2SnCl + Fe_2O_3 = Sn_2O_3 + 2FeCl.$$

The sesquioxide thus obtained is a slimy grey matter, and usually yellow from adhering oxide of iron. Ammonia dissolves it easily, and without residue, a character which distinguishes this oxide from the protoxide of tin, the latter being insoluble, or nearly so, in that menstruum. Sesquioxide of tin is dissolved by concentrated hydrochloric acid; the taste of the solution is not metallic. It is distinguished from a salt of the bioxide of tin, by producing the purple precipitate with chloride of gold. A sesquisulphide exists, corresponding with this oxide. The salts of sesquioxide of tin have not been examined.

Bioxide of tin, Stannic oxide, SnO_2, 74·82 *or* 935·25.—This constitutes the common ore of tin, which is generally crystallised. The crystals of *tin-stone* are sometimes brownish-yellow and translucent, at other times dark brown and almost black, and contain small quantities of the protoxides of iron and manganese. Their primitive form is an obtuse octohedron with a square base; their density from 6·92 to 6·96. Bioxide of tin in this state does not dissolve in acids, unless previously ignited with an alkali. Anhydrous stannic oxide may be obtained in colourless crystals derived from a right rhomboïdal prism, which scratch glass, and have a density of 5·72, by decomposing vapour of bichloride of tin with water at a red heat. These crystals are isomorphous with one of the native varieties of titanic acid (brookite), whereas the crystals of native tin-

stone are isomorphous with another variety of titanic acid (rutile).

Bioxide of tin is susceptible of two modifications called *stannic* and *metastannic* acid, distinguished from one another by the proportions of water and metallic oxide with which they combine.

Stannic acid, or *Hydrated stannic oxide*, $SnO_2.HO$, is obtained by decomposing bichloride of tin with water, or by precipitating a soluble stannate with an acid. It is white, gelatinous, insoluble in water, but dissolves readily in dilute acids. A moderate heat converts it into metastannic acid. At a red heat, it gives off all its water, and becomes very hard.

Solutions of stannic oxide in acids (the hydrated bichloride for example), are decomposed by *zinc* and *cadmium*, the tin being precipitated in an arborescent form. *Hydrosulphuric acid* and *sulphide of ammonium* throw down the yellow bisulphide soluble in alkalies and in sulphide of ammonium. *Ammonia* throws down a white bulky hydrate, soluble with some turbidity in a large excess of ammonia. The presence of tartaric acid prevents the precipitation. *Potash* throws down a white bulky hydrate (probably containing potash), easily soluble in excess. *Carbonate of potash* gives a white precipitate, consisting, according to Fremy, of stannate of potash, which dissolves in excess of the reagent, but separates completely after a while. *Bicarbonate of potash* and *sesquicarbonate of ammonia* throw down the hydrated oxides, insoluble in excess of the reagent. Chloride of gold gives no precipitate with stannic salts.

All salts of tin are easily reduced to the metallic state when heated on charcoal before the blowpipe with carbonate of soda or cyanide of potassium.

The compounds of stannic acid with bases are represented by the general formula $MO.SnO_2$. The stannates of the alkalies crystallise readily, and may be obtained in the anhydrous state. They are prepared by dissolving stannic acid in

alkalies, or by calcining metastannic acid or the metastannates in contact with an excess of base. *Stannate of potash*, $KO.SnO_2+4HO$, is white, very soluble in water, insoluble in alcohol; it crystallises in oblique rhomboïdal prisms, which are transparent, sometimes very large, and slowly absorb moisture from the air. It has a caustic taste and strong alkaline reaction. Water appears to decompose it after a while into potash and metastannate of potash. It is precipitated from its solution by nearly all soluble salts, even by those of potash, soda and ammonia. *Stannate of soda*, $NaO.SnO_2 + 4HO$, resembles the potash-salt, and is obtained in a similar manner. It crystallises in hexagonal tables, dissolves in cold more readily than in hot water, is insoluble in alcohol, and has a strong alkaline reaction (Fremy).

The stannates of all other bases are insoluble in water, and may be formed by double decomposition. The sesquioxide of tin may be regarded as a stannate of stannous oxide, $SnO.SnO_2$ (Fremy).

Metastannic acid, Sn_5O_{10}.—Tin treated with strong nitric acid is completely transformed into a white powder, which, when dried in the air at ordinary temperatures, contains $Sn_5O_{10}.10HO$; after being heated for some time to 212°, it is reduced to $Sn_5O_{10}.5HO$. It is white, crystalline, insoluble in water, and in dilute nitric acid and sulphuric acid. Monohydrated sulphuric acid dissolves it in considerable quantity, forming a compound which is not decomposed by water or alcohol. It dissolves in dilute hydrochloric acid, forming a liquid, which, when treated with excess of acid, yields a white amorphous precipitate, differing considerably from hydrated bichloride of tin. Metastannic acid also combines with certain organic acids. The acid prepared with nitric acid is completely insoluble in ammonia, but when dissolved in potash and precipitated by an acid, it becomes gelatinous and soluble in ammonia; in that state, it contains more water than in the crystalline state; but by the slightest desiccation, or even by

boiling for a few minutes, it gives up part of its water, and is reconverted into the modification insoluble in ammonia. Other hydrates of metastannic acid appear also to exist, possessing different properties.

The *metastannates* are represented by the general formula $(MO.4HO.)\ Sn_5O_{10}$. They can only exist in the hydrated state, being decomposed when deprived of their basic water. The potash and soda-salts, heated with excess of base, are transformed into stannates. They are soluble in basic water. The other metastannates are insoluble, and are obtained by double decomposition. *Metastannate of potash*, $(KO.4HO).Sn_5O_{10}$, is prepared by dissolving metastannic acid in cold potash; it may be precipitated in the solid state by adding pieces of potash to the liquid. It is gummy, uncrystallisable, and strongly alkaline. At a red heat, it gives off its water and is decomposed; the calcined mass, digested in water, yields up all its alkali and leaves insoluble metastannic acid. The *soda-salt*, $(NaO.4HO).Sn_5O_{10}$, closely resembles the potash-salt, but is crystalline, dissolves slowly in water, and is decomposed by boiling water. *Metastannate of stannous oxide*, $(SnO.4HO).Sn_5O_{10}$, is obtained by placing metastannic acid in contact with protochloride of tin. It is yellow, and insoluble in water; when heated in contact with the air, it is transformed into anhydrous stannic acid (Fremy).

Oxide of tin is employed in the preparation of the white glass known as enamel; and the ignited and finely levigated oxide forms *jeweller's putty*, which is used in polishing hard objects. The hydrated oxide resembles alumina in forming insoluble compounds with the organic colouring matters; hence its salts are much prized as mordants.

Bisulphide of tin, Stannic sulphide, SnS_2, is precipitated from stannic salts, of a dull yellow colour, by hydrosulphuric acid gas. Prepared in the dry way, by igniting a mixture of stannic oxide, sulphur, and sal-ammoniac in a covered crucible, it forms the *aurum musivum* or *mosaic gold* of the alchemists. In

this operation, the sal-ammoniac is indispensable, although it seems to serve no other purpose than to prevent the elevation of temperature which results from the sulphuration. Mosaic gold when well prepared has the yellow colour of gold, and consists of brilliant translucent scales, which are soft to the touch. No acid dissolves it, except aqua-regia. It is decomposed by dry chlorine, yielding the compound $SnCl_2.SCl_2$.

Bichloride of tin, Permuriate of tin, Stannic chloride, $SnCl_2$; 129·82 *or* 1622·75.—The anhydrous bichloride of tin, known as the fuming liquor of Libavius, is procured by distilling, at a gentle heat, a mixture of 4 parts of corrosive sublimate and 1 part of tin in filings, or tin amalgamated with a little mercury, and then reduced to powder. A colourless, highly limpid liquid is found in the condenser, which fumes strongly in humid air. The bichloride boils at 248°; the density of its vapour, observed by Dumas, is 9·1997. It forms a solid saline mass with one third of its weight of water, and dissolves in a larger quantity of water. The same salt is obtained in solution, by conducting a stream of chlorine gas into a strong solution of the protochloride of tin, till the latter is saturated, which is shown by the solution ceasing to precipitate mercury from a solution of corrosive sublimate. A solution of this salt extensively used in dyeing, and known as the nitromuriate of tin, is generally prepared by oxidising crystallised protochloride of tin with nitric acid; or by dissolving tin in a mixture of hydrochloric and nitric acids, avoiding any considerable elevation of temperature.

Ammonio-bichloride of tin, $SnCl_2.NH_3$ *or* $(NH_3Sn)Cl_2$.—Anhydrous bichloride of tin absorbs ammoniacal gas, and forms a white powder, which may be sublimed without decomposition; after sublimation it is entirely soluble in water (Rose).

Chlorosulphide of tin, $SnS_2.2SnCl_2$. — Hydrosulphuric acid gas is rapidly absorbed by bichloride of tin, with formation of hydrochloric acid gas:

$$3SnCl_2 + 2HS = SnS_2.2SnCl_2 + 2HCl.$$

The compound obtained by perfect saturation with hydrosulphuric acid is a yellowish or reddish liquid, heavier than water. When heated, it gives off bichloride of tin, and leaves the bisulphide (Dumas).

Bichloride of tin and sulphur, $SnCl_2.2SCl_2$.—Formed by the action of chlorine gas on bisulphide of tin at ordinary temperatures:

$$SnS_2 + 6Cl = SnCl_2.2SCl_2.$$

Large yellow crystals, which fuse when heated, and sublime without decomposition; they fume in the air more strongly than the bichloride.

Bichloride of tin with Pentachloride of phosphorus, $2SnCl_2.PCl_5$.—When a mixture of the last-described compound with terchloride of phosphorus is moderately heated in a stream of hydrochloric acid gas, a rapid action takes place, and this compound is formed, together with other products:

$$2(SnCl_2.2SCl_2) + 3PCl_3 = 2SnCl_2.PCl_5 + 2PCl_5 + 2S_2Cl.$$

If the retort in which the action takes place is connected with a receiver surrounded with ice, a pasty, yellowish mass collects in the receiver, and an amorphous white body remains in the retort. On heating the yellowish mass to between 212° and 250°, dichloride of sulphur escapes, and there remains a mixture of pentachloride of phosphorus with the double chloride, identical, in fact, with the amorphous white mass in the retort. On heating this mixture to a temperature between 284° and 320°, the pentachloride of phosphorus is also driven off, leaving the double chloride, which sublimes between 392° and 428°, in highly lustrous colourless needles, which, however, soon crumble to an amorphous powder, even when kept in close vessels. The compound fumes strongly in the air, and rapidly absorbs water, being thereby converted into transparent colourless crystals containing water of crystallisation.*

* Casselmann, Ann. Ch. Pharm. lxxxiii. 257.

Bichloride of tin with Oxychloride of phosphorus, $2SnCl_2 + PO_2Cl_3$. — Obtained by the action of oxychloride of phosphorus on bichloride of tin: if an excess of either substance is present, the compound separates in large isolated crystals. It has a peculiar odour, melts at 131°, and boils at 356°, and distils without alteration if kept from contact with moist air. It fumes in the air and is decomposed by water. When oxychloride of phosphorus comes in contact in a close vessel with the compound $SnCl_2.2SCl_2$, the whole dissolves, forming a yellowish liquid, from which, after a while, the compound $2SnCl_2 . PO_2Cl_3$ crystallises; and above the crystals there remains a yellow liquid, probably SCl_2 (Casselmann).

Bichloride of tin with Phosphuretted hydrogen, $3SnCl_2.PH_3$. — These two bodies unite without production of hydrochloric acid; the compound is solid (Rose).

Bichloride of tin with potassium, $SnCl_2.KCl$. — The solution of bichloride of tin, when mixed with an equivalent quantity of chloride of potassium and evaporated, yields this double salt in anhydrous regular octohedrons having a vitreous lustre. A similar double salt is formed with chloride of ammonium.

A *sulphate* and *nitrate of bioxide of tin*, have been crystallised; this base forms no carbonate.

Both the *sulphide* and *bisulphide of tin* act as sulphur-acids, combining with alkaline sulphide. The bisulphide of tin dissolves with digestion in sulphide of sodium, and the concentrated solution yields fine crystals of the salt, $2NaS.SnS_2 + 12HO$. By gradually adding tin to melted pentasulphide of sodium, treating the resulting mass with water, and then filtering and evaporating, yellowish octohedral crystals are obtained, containing $NaS.SnS_2 + 2HO$.* The bisulphide of tin is found combined with the subsulphides of copper and iron, forming *tin pyrites*, a rare mineral, $2Fe_2S.SnS_2 + 2Cu_2S.SnS_2$.

Alloys of tin. — Tin alloyed with small quantities of anti-

* Kühn, Pogg. Ann. lxxxv. 293.

mony, copper, and bismuth, forms the best kind of pewter, possessing the peculiar whiteness of metallic tin. The most fusible compound of tin and bismuth is that of an atom of each metal, Bi.Sn; it melts at 289·4° (Rudberg). When the metals are mixed in other ratios, a portion first congeals at a higher temperature, separating from the compound mentioned, which remains liquid till the temperature falls to 289·4°. Although tin precipitates copper from its solutions in acids, yet it is possible to precipitate tin upon copper, and to cover the latter with tin, as is proved by the tinning of pins. Tin is dissolved in a mixture of 1 part of bitartrate of potash, 2 of alum, 2 of common salt, and a certain quantity of water, and the pins which consist of brass wire are introduced at the boiling temperature. The pins undergo no change in this liquor, supposing it to contain no undissolved tin, but the moment a fragment of tin touches the pins, all those in contact with each other are tinned. Dr. Odlings finds that pure copper boiled in a moderately dilute and rather acid solution of stannous chloride, also becomes coated with tin.*

ESTIMATION OF TIN, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Tin is estimated in the state of bioxide, a compound which contains 78·62 per cent. of the metal. If the tin is united with other metals in the form of an alloy, the alloy must be treated with nitric acid of sp. gr. about 1·3. The tin is then converted into bioxide, while the other metals (with the exception of antimony) are dissolved by the acid. The oxide of tin must then be thoroughly washed, afterwards dried, ignited, and weighed. To insure complete oxidation, the alloy should be finely divided.

When the tin is in solution in hydrochloric acid (which is its usual solvent) it must first be precipitated as a sulphide

* Chem. Soc. Qu. J. ix. 291.

by hydrosulphuric acid, and the sulphide then converted into bioxide by roasting in an open porcelain crucible, a small quantity of nitric acid being added to insure complete oxidation.

Precipitation by hydrosulphuric acid serves also to separate tin from all metals which are not thrown down by that reagent from their acid solutions.

From *cadmium, copper,* and *lead,* tin may be separated by treating the solution with a slight excess of ammonia, and then adding sulphide of ammonium containing excess of sulphur. All the metals are thereby converted into sulphides, but the sulphide of tin dissolves, while the others are left undissolved.

Volumetric estimation of tin.—The following method of estimating the amount of tin in the commercial protochloride is given by Dr. Penny*; it is based on the conversion of protochloride of tin into bichloride by the action of chromic acid in presence of free hydrochloric acid:

$$3SnCl + KO.2CrO_3 + 7HCl = 3SnCl_2 + KCl + Cr_2Cl_3 + 7HO.$$

The solution of the tin-salt is mixed with a sufficient quantity of hydrochloric acid and gently heated, and a solution of bichromate of potash gradually added, till a drop of the liquid added to acetate of lead (a solution of 1 part of that salt in 8 parts of water being scattered in large drops on a porcelain plate) produces a faint yellow colour; or till the liquid produces a dark brown or red colouring in an acidulated mixture of sulphocyanide of potassium and a pure protosalt of iron. With the commercial solution of the protochloride of tin, the contrary method is adopted; that is to say, the tin solution, diluted and reduced to a definite volume, is poured into a solution of bichromate of potash containing a known weight of that salt. Penny finds, by direct experiments, that 83·2 parts of pure bichromate of potash correspond to 100 parts of tin.

* Chem. Soc. Qu. J. iv. 249.

SECTION II.

TITANIUM.

Eq. 24·33 *or* 303·7; Ti.

This metal was discovered in 1791, by Mr. Gregor of Cornwall, and afterwards by Klaproth, who gave it the name titanium. In the form of titanic acid it constitutes several minerals, as rutile, anatase, menachanite, &c.; and as titanate of protoxide of iron, it forms ilmenite and other species.

When titaniferous iron-ores are smelted in the blast furnace, small cubic crystals of a bright copper colour are found on the slag which adheres to the lower part of the furnace. These crystals were long supposed to be metallic titanium; but Wöhler* has shown that they also contain carbon and nitrogen, being, in fact, a compound of cyanide of titanium with nitride of titanium, $CyTi.3NTi_3$. Pure titanium is obtained by heating the double fluoride of potassium and titanium with potassium in a covered crucible. The metal is then set free with vivid incandescence, and the fluoride of potassium may be removed by washing with water. Titanium thus obtained is a dark green, heavy, amorphous powder, which does not exhibit any shade of copper colour, even after pressure; under the microscope it appears as a cemented mass, having the colour and lustre of iron. Metallic titanium is also obtained by mixing titanic acid with one-sixth of its weight of charcoal and exposing it to the strongest heat of a wind-furnace. It was thus obtained in the form of a copper-coloured or gold-coloured powder by Vauquelin, Lampadius, and others; but possibly the charcoal which they used may have contained nitrogen, and that element united with the reduced metal.

* Ann. Ch. Pharm. lxxiii. 34.; Chem. Soc. Qu. J. ii. 352.

Pure titanium (prepared from the double fluoride) burns with great splendour when heated in the air, and, if sprinkled into a flame, is consumed, with brilliant scintillations, at a considerable distance above the point of the flame. When heated to redness in oxygen-gas, it burns with a splendour resembling a discharge of electricity. In chlorine-gas it exhibits similar phenomena, requiring also the aid of heat to set it on fire. Mixed with red lead and heated, it burns with such violence that the mass is thrown out of the vessel, with loud detonation. Titanium does not decompose water at ordinary temperatures, but on heating the water to the boiling point, hydrogen begins to escape. Warm hydrochloric acid dissolves titanium with brisk evolution of hydrogen. Ammonia added to the solution throws down a black oxide; and, on heating the liquid, hydrogen is evolved, and the precipitate first turns blue, and is afterwards converted into white titanic acid.

Titanium forms three compounds with oxygen: viz. the *protoxide*, TiO, whose composition is, however, doubtful; the *sesquioxide*, Ti_2O_3; and *titanic acid*, TiO_2.

Protoxide of titanium, TiO, 32·33. *or* 403·7 — Is formed when titanic acid is exposed in a charcoal crucible, to the highest temperature of a wind-furnace. Where the acid was in contact with the charcoal, a thin coating of metallic titanium is formed; but within, it is changed into a black mass, which is insoluble in all acids, and not otherwise affected by them, and is oxidated with difficulty when heated in contact with air, or by fusion with nitre. Protoxide of titanium is also obtained by the moist way, in the form of a deep purple powder, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid; but it alters so quickly by absorption of oxygen, that no opportunity has yet been obtained of studying its properties. The composition assigned to it above is, therefore, hypothetical. The blue powder is,

perhaps, a compound of protoxide of titanium with oxide of zinc or iron.

Sesquioxide of titanium, Ti_2O_3.—When anhydrous titanic acid is strongly ignited in a current of hydrogen gas, it becomes black and loses considerably in weight. From a determination of the actual loss of weight, Ebelmen concludes that sesquioxide of titanium is produced. The residue is not acted upon by nitric or hydrochloric acid, but dissolves in sulphuric acid, forming a violet solution.*

Titanic acid, TiO_2, 40·33 *or* 503·7.— In the mineral rutile, titanic acid is crystallised in the form of tinstone, the link by which tin is connected with titanium. Again, ilmenite and other varieties of titanate of iron, $FeO.TiO_2$ are isomorphous with sesquioxide of iron; and thus tin comes to be connected through titanium with the last order of metals. But titanic acid is dimorphous, and crystallises, in anatase, in an unconnected form. The best method of obtaining pure titanic acid is to fuse titanate of iron, reduced to powder and levigated with sulphur. The sulphur has no action upon the titanic acid, but converts the protoxide of iron into a sulphide of iron, which is dissolved by hydrochloric acid. If iron is still retained by the titanic acid, the latter is heated in a stream of hydrosulphuric acid gas, by which every particle of iron is converted into sulphide, and then removed by hydrochloric acid.

Titanic acid is a white powder, which acquires a yellow tint by exposure to a high temperature; it is infusible and insoluble in water. Titanic acid is considerably analogous in properties to silica; like that acid it has a soluble modification, formed by igniting titanic acid with an alkaline carbonate, which is soluble in dilute hydrochloric acid. The acid solution of titanic acid gives an orange-red precipitate with an infusion of gall-nuts, which is characteristic of titanic acid.

* Ann. Ch. Phys. [3.] xx. 385.

On neutralising the acid solution with ammonia, the soluble modification of titanic acid is thrown down as a white gelatinous precipitate. When this precipitate is dried and heated, it glows, and the titanic acid is then no longer soluble in acids. When a solution of bichloride of titanium, or of the sulphate of titanic acid in water, is boiled for some time, titanic acid precipitates in the insoluble modification.

Titanic acid mixed with borax, or better with phosphorus-salt, forms in the outer blowpipe-flame a colourless glass, but in the inner flame, a glass which is yellow while hot, but assumes a violet colour on cooling. The same character is exhibited by those salts of titanic acid whose bases do not themselves impart any colour to the bead. If the titanic acid contains iron, the colour of the bead is brown-red or blood-red instead of violet. Many titanates yield the blue colour only with phosphorus-salt, not with borax. The colour is produced more readily by heating the substance on charcoal than on platinum wire. The above characters suffice to distinguish titanic acid from all other substances.

Bisulphide of titanium, TiS_2, was discovered by Rose, who formed it by passing the vapour of bisulphide of carbon over titanic acid, in a porcelain tube maintained at a bright red heat.

Bichloride of titanium, $TiCl_2$, was formed by Mr. George of Leeds, by transmitting chlorine over metallic titanium at a red heat. It is a transparent colourless liquid, resembling bichloride of tin, and boiling a little above 212°. The density of its vapour is 6·615 (Dumas). Bichloride of titanium combines with ammonia, and forms a white saline mass, $TiCl_2.2NH_3$. Metallic titanium is most easily obtained by heating this compound to redness. Bichloride of titanium also absorbs phosphuretted hydrogen, and forms a dry brown powder. From this compound when heated, a lemon-yellow sublimate rises, which Rose found to contain 3 atoms of bichloride of titanium, combined with 1 atom of a compound of phosphuretted hydrogen and hydrochloric acid, analogous to

sal-ammoniac, but which could not be isolated. Bichloride of titanium combines with the alkaline chlorides, forming double salts, which are colourless and capable of crystallising. It also combines with chloride of cyanogen, forming a yellow crystalline compound containing $CyCl . 2TiCl_2$, and with anhydrous hydrocyanic acid, forming the compound $HCy . TiCl_2$, a yellow pulverulent substance which sublimes below 212°, in transparent, shining, lemon-yellow crystals.

Bromide of titanium, $TiBr_2$, is obtained by passing bromine vapour over an intimate mixture of titanic acid and carbon, heated to bright redness, and distilling the resulting brown liquid with excess of mercury to remove free bromine. It is an amber-yellow crystalline body of specific gravity 2·6. It melts at 102°, and boils at 356°. It attracts moisture with the greatest avidity, and is converted into titanic and hydrobromic acids (F. B. Duppa).

A volatile *bifluoride of titanium*, TiF_2, was obtained by Unverdorben, by distilling titanic acid in a platinum apparatus with fluor spar in powder and fuming sulphuric acid.

A definite *sulphate of titanic acid*, $TiO_2 . SO_3$, is obtained by dissolving titanic acid in sulphuric acid, and evaporating to dryness at a heat below redness.

Nitrides of titanium.—H. Rose, by heating the double chloride of titanium and ammonium in ammoniacal gas, or by heating the ammonio-chloride of titanium, $2NH_3 . TiCl_2$, with sodium, obtained a copper-coloured substance which he supposed to be metallic titanium, but which Wöhler has shown to consist of nitride of titanium, Ti_3N_2, or more probably $Ti_6N_4 = 3TiN . Ti_3N$; it contains 28 per cent. of nitrogen. This compound is redder than the cubic crystals of the blast-furnaces, which have a tinge of yellow. Another nitride of titanium, TiN, is produced when titanic acid is strongly heated in a stream of ammoniacal gas. Its powder is dark violet with a tinge of copper-colour; in small pieces it exhibits a violet copper-colour and metallic lustre. A third

nitride, Ti_5N_3, or more probably $2TiN \cdot Ti_3N$, is formed when Rose's titanium is subjected to the action of a stream of hydrogen at a strong red heat. It has a brassy or almost gold-yellow colour and a metallic lustre. It is also obtained (mixed however with carbon) when titanic acid is heated to redness in a stream of cyanogen gas or hydrocyanic acid vapour; no cyanide of titanium is formed in this reaction. All these three nitrides of titanium sustain without decomposition, a temperature at least equal to that of melting silver. Mixed in the state of powder with the oxides of copper, lead, or mercury, and heated, they emit a lively sparkling flame, and reduce the oxides to the metallic state. When fused with hydrate of potash, they give off ammoniacal gas (Wöhler).

Nitrocyanide of titanium, $C_2NTi \cdot 3Ti_3N$. — This is the copper-coloured compound already spoken of as occurring in the iron furnaces, and formerly mistaken for metallic titanium. Its formation appears to be connected with that of cyanide of potassium, so constantly observed in the blast-furnaces. It sometimes occurs in very large masses; in a furnace at Rübeland in the Hartz, a mass of it was found, weighing 80 pounds. This compound forms cubic crystals harder than quartz, and of specific gravity 5·3. It contains 18 per cent. of nitrogen and 4 of carbon. In its chemical characters, it resembles the nitrides just described, giving off ammonia when heated with potash, and reducing the oxides of lead, copper, and mercury, when heated with them. A similar product may be formed by placing a mixture of titanic acid and ferrocyanide of potassium in a well closed crucible, and exposing it for an hour to a heat sufficient to melt nickel. (Wöhler.)

ESTIMATION OF TITANIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Titanium is always estimated in the form of titanic acid. This compound is best precipitated from its solutions in acids by ammonia, which throws it down in the form of a very bulky precipitate, resembling hydrate of alumina. A great excess of ammonia must be avoided, as it would redissolve a small portion of the titanic acid. The precipitate after ignition contains 60 per cent. of titanium.

If the titanic acid, after precipitation by ammonia, is to be redissolved in acids, which is sometimes necessary in order to separate it from other metals, great care must be taken in the precipitation to avoid all rise of temperature, and the precipitate must be washed with cold water, because heat has the effect of rendering titanic acid more or less insoluble in acids.

Titanic acid may also in some cases be separated from its acid solutions by boiling; from the solution in sulphuric acid, complete precipitation is effected by this method; but when hydrochloric acid is the solvent, a small portion of titanic acid always remains in solution after boiling.

Protoxide of titanium is precipitated from its solutions by ammonia, and the precipitate, after standing from 24 to 36 hours, is converted, with evolution of hydrogen, into titanic acid, in which form it may be estimated.

From the *alkalies* and *alkaline earths*, titanic acid may be separated by ammonia, the solution in the latter case being carefully excluded from the air. Baryta may also be separated by sulphuric acid.

Titanic acid is separated from *magnesia* by boiling, if the two are dissolved in sulphuric acid, and by precipitation with carbonate of baryta, when hydrochloric acid is the solvent.

The separation from *alumina* and *glucina* is also effected by boiling the sulphuric acid solution.

From the metals which are precipitated as sulphides by sulphide of ammonium, viz., *manganese, iron, cobalt, nickel,* and *zinc,* titanic acid is separated by mixing the acid solution with tartaric acid and excess of ammonia (which then forms no precipitate), and adding sulphide of ammonium, which precipitates everything but the titanic acid. The filtered solution is then evaporated to dryness, and the residue ignited in a platinum crucible to expel ammoniacal salts and burn away the carbon of the tartaric acid. As this carbonaceous matter is very difficult to burn, the ignition should either be performed in a muffle furnace, or a stream of oxygen should be very gently directed into the crucible. The residue consists of titanic acid, which may then be weighed.

From *cadmium, copper, lead,* and *tin,* titanium is easily separated by hydrosulphuric acid.

SECTION III.

CHROMIUM.

Eq. 26·8 *or* 335; Cr.

This metal, so remarkable for the variety and beauty of its coloured preparations, was discovered by Vauquelin in 1797, in the red mineral now known as chromate of lead. It has since been found in other minerals, more particularly *chrome-iron* ($FeO . Cr_2O_3$), a mineral which many countries possess in considerable quantity. It is from this ore that the compounds of chromium, used in the arts, are actually derived. The metal may be procured by the reduction of its oxide, in the usual way; but the reduction is as difficult as that of manganese. Chromium is a greyish-white metal, of density 5·9, very difficult to fuse, and not magnetic. It does not undergo oxidation in the air. It dissolves in hydrofluoric acid with evolution of hydrogen. Chromium is also obtained

as a brown powder, when sesquichloride of chromium is heated in ammoniacal gas (Liebig).

Chromium forms several compounds with oxygen; viz. *protoxide of chromium*, or *chromous oxide*, CrO, isomorphous with ferrous oxide, &c.; *sesquioxide of chromium*, or *chromic oxide*, Cr_2O_3, isomorphous with ferric oxide and alumina; and *chromic acid*, CrO_3, isomorphous with sulphuric acid; also a *chromoso-chromic oxide*, Cr_3O_4, or $CrO.Cr_2O_3$, and four oxides intermediate between chromic oxide and chromic acid, which may, in fact, be regarded as chromates of chromic oxide; viz. *monochromate of chromic oxide*, or $Cr_2O_3.CrO_3 = Cr_3O_6$; the *bichromate*, $Cr_2O_3.2CrO_3 = Cr_4O_9$; the neutral chromate, $Cr_2O_3.3CrO_3 = Cr_5O_{12}$, and the acid chromate, $Cr_2O_3.4CrO_3 = Cr_6O_{15}$.

Protoxide of chromium, Chromous oxide, CrO; 34·8 or 435.—This oxide probably exists in chrome-iron, and in pyrope. It is precipitated in the form of a hydrate by the action of potash on a solution of the protochloride. The anhydrous protoxide has not yet been obtained. The hydrate is very unstable, decomposes water, even at ordinary temperatures, and if the air be not excluded by filling the apparatus with hydrogen, is converted, almost as soon as formed, into chromoso-chromic oxide Cr_3O_4, with evolution of hydrogen (Péligot). It is yellow when recently precipitated, brown when dry, and may be preserved unaltered in dry air. When ignited it gives off hydrogen, and the oxygen thereby liberated converts the remaining protoxide into sesquioxide (Moberg).

Hydrated chromous oxide is insoluble in dilute acids, but dissolves slowly in strong acids. The chromous salts are best prepared by mixing a solution of the protochloride with the corresponding potash or soda salts, access of air being carefully prevented. They are generally of a red colour, sometimes inclining to blue; dissolve but sparingly in cold water, but more readily in hot water. Like ferrous salts, they dissolve large quantities of nitric oxide, forming dark brown solutions.

Protochloride of chromium, Chromous chloride, CrCl; 62·3 *or* 778·75.—Obtained by passing hydrogen gas over perfectly anhydrous sesquichloride of chromium very gently heated, as long as hydrochloric acid gas continues to escape. The hydrogen must be previously freed from all traces of oxygen by passing it through a solution of protochloride of tin in caustic potash, then through tubes containing sulphuric acid and chloride of calcium, and lastly over red-hot metallic copper. The protochloride is also formed by passing dry chlorine gas over a red-hot mixture of charcoal and chromic oxide. The first method yields the protochloride in the form of a white, velvety substance, retaining the form of the sesquichloride from which it has been formed; the second method yields it in fine white crystals, usually mixed, however, with chromic oxide, chromic chloride, and charcoal.

Protochloride of chromium dissolves in water, with evolution of heat, forming a blue solution, which rapidly turns green when exposed to the air or to chlorine gas. With *potash* it forms a dark brown precipitate (yellow, according to Moberg, if the air be completely excluded) of hydrated chromous oxide, which, however, quickly changes to light brown chromoso-chromic oxide, with evolution of hydrogen. *Ammonia* forms a greenish white precipitate, without evolution of hydrogen. With ammonia and sal-ammoniac, a blue liquid is formed which turns red on exposure to the air. *Sulphide of ammonium* or *potassium* forms a black precipitate of chromous sulphide. The solution of protochloride of chromium is one of the most powerful deoxidising agents known. With a solution of *monochromate of potash,* it forms a dark brown precipitate of chromoso-chromic oxide, which, however, disappears on the addition of an excess of the protochloride, and forms a green solution. It precipitates *calomel* from a solution of corrosive sublimate. With *cupric salts,* it forms at first a white precipitate of cuprous chloride; but when added in excess throws down red cuprous oxide. It instantly converts *tungstic*

acid into blue oxide of tungsten, and precipitates *gold* from the solution of the chloride.

Chromous carbonate is formed by adding a solution of the chloride to carbonate of potash; its precipitate is red or red-brown, if the alkaline solution is hot, but in the form of dense yellow or bluish green flakes, if it is cold; the precipitate appears, however, to have the same composition in all cases (Moberg).

Chromous sulphite is obtained by double decomposition in the form of a brick-red precipitate, which becomes bluish-green on exposure to the air (Moberg).

Chromous sulphate.—When the metallic powder obtained by treating sesquichloride of chromium with potassium is treated with dilute sulphuric acid, hydrogen is evolved, and a solution obtained which exhibits the characters of a chromous salt (Péligot).

Chromoso-chromic oxide, $Cr_3O_4 = CrO \,.\, Cr_2O_3$.—Formed when the protoxide comes in contact with water, and consequently at the moment of its precipitation by potash, from a solution of the protochloride. After washing with water and drying in vacuo, it has the colour of Spanish tobacco. It is but feebly attacked by acids. The hydrate is composed of $Cr_3O_4 \,.\, HO$; when heated, it is converted into chromic oxide with evolution of hydrogen.

Sesquioxide of chromium, Chromic oxide, 77·6 or 970.—This oxide exists in chrome-iron, but is not immediately derived from that mineral. When chromate of mercury, the orange precipitate obtained on mixing nitrate of mercury and chromate of potash, is strongly ignited, chromic oxide remains as a powder of a good green colour. Chromic oxide is also obtained, by deoxidising the chromic acid of bichromate of potash in various ways; by ignition with sulphur, for instance, or by igniting together 1 part of bichromate of potash with $1\frac{1}{2}$ parts of sal-ammoniac and 1 part of carbonate of potash, whereby chloride of potassium and sesquioxide of chromium

are formed, the chromic acid losing half its oxygen, which is converted into water by the hydrogen of the ammonia. Another process, interesting from affording the oxide in the state of crystals, is to pass the vapour of chlorochromic acid (CrO_2Cl) through a tube heated to whiteness, when oxygen and chlorine gases are disengaged, and chromic oxide attaches itself to the surface of the tube. The crystals have a metallic lustre, and are of so deep a green as to appear black; they have the same form as specular iron ore, a density of 5·21, and are as hard as corundum (Wöhler). The ignited oxide is not soluble in acids; heated with access of air, and in contact with an alkali, it absorbs oxygen and is converted into chromic acid. Fused with borax or other vitreous substances, sesquioxide of chromium produces a beautiful green colour; it is the colouring matter of the emerald, and is employed to produce a green colour upon earthenware. Sesquioxide of chromium (and not chromic acid) is also the colouring matter of *pink colour* applied to stoneware. This substance is formed by strongly igniting a mixture of 100 parts of bioxide of tin, 33 parts of chalk, and not more than one part of sesquioxide of chromium.*

To obtain the same oxide in the hydrated state, a solution of bichromate of potash is brought to the boiling point, and hydrochloric acid and alcohol added alternately in small quantities, till the solution passes from a red to a deep green colour, and no longer effervesces from escape of carbonic acid gas, on addition of either the acid or alcohol. In this experiment, the chromic acid liberated by the hydrochloric acid, is deprived of half its oxygen by the hydrogen and carbon of the alcohol, and the resulting sesquioxide of chromium is dissolved by the excess of hydrochloric acid pre-

* Malaguti, Ann. Ch. Phys. [3.] lxi. p. 433. Mr. O. Sims finds that sesquioxide of iron and bioxide of manganese may be substituted for oxide of chromium in pink colour, so that the coloration of that substance is of a very peculiar character.

sent, and in fact converted into the corresponding sesquichloride of chromium. Many other organic substances may be used in place of alcohol in this experiment, such as sugar, oxalic acid, &c. The reduction may also be effected by hydrosulphuric acid or even by hydrochloric acid alone, if added in sufficient excess; in this last case, sesquichloride of chromium and chloride of potassium are then formed, and part of the chlorine escapes as gas; thus:

$$KO.2CrO_3 + 7HCl = KCl + Cr_2Cl_3 + 7HO + 3Cl.$$

The oxide of chromium is precipitated from the green solution by ammonia, and falls as a pale bluish-green hydrate. The same oxide is obtained more directly, when to a boiling solution of bichromate of potash a hot solution of pentasulphide of potassium is added, the chromic acid then giving half its oxygen to the sulphur.

Hydrated chromic oxide is soluble in acids, and forms salts. It is also dissolved by potash and soda, but not to a great extent by ammonia. Its salts have a sweet taste, and are poisonous. The oxide itself becomes of a greener colour when dried, and loses water. A moderate heat affects its relations to acids, the sulphate of the heated (or green) oxide not forming a double salt, for instance, with sulphate of potash. When heated to redness, it glows, or undergoes the same change as zirconia, bioxide of tin, and many other hydrated oxides when made anhydrous; becomes denser, assumes a pure green colour, and ceases to be soluble in acids.

The salts of chromic oxide exhibit two different modifications, green and violet; some acids, *e. g.*, sulphuric and hydrochloric, produce both modifications; others only one. *Ammonia* produces, in solutions of the green salts, a bluish-gray precipitate, but in solutions of the violet salts, a greenish-gray precipitate, both of which, however, yield green solutions when dissolved in sulphuric or hydrochloric acid (Regnault); according to H. Rose, however, the precipitate is bluish-gray in both

cases. The liquid above the precipitate has a reddish colour, and contains a small quantity of chromic acid. *Potash* and *soda* form similar precipitates, which dissolve in excess of the alkali, forming green solutions from which the chromic oxide is precipitated by boiling. The *alkaline carbonates* form greenish precipitates (violet by candle-light), which dissolve to a considerable extent in excess of the reagent. *Hydrosulphuric acid* forms no precipitate ; *sulphide of ammonium* throws down the hydrated sesquioxide.

Zinc, immersed in a solution of chrome-alum or sesquichloride of chromium excluded from the air, gradually reduces the chromic salt to a chromous salt, the liquid after a few hours acquiring a fine blue colour, and hydrogen being evolved by decomposition of water. If the zinc be left in the liquid after the change of colour from green to blue is complete, hydrogen continues to escape slowly, and the liquid after some weeks or months, is found no longer to contain chromium, the whole of that metal being precipitated in the form of a basic salt, and its place taken by zinc. *Tin*, at a boiling heat, likewise reduces the chromic salt to a chromous salt, but only to a limited extent ; and on leaving the liquid to cool after the action has ceased, a contrary action takes place, the protochloride of chromium decomposing the protochloride of tin previously formed, reducing the tin to the metallic state, and being itself reconverted into sesquichloride. *Iron* does not reduce chromic salts to chromous salts, but merely precipitates a basic sulphate of chromic oxide, or an oxychloride, as the case may be.*

Sesquioxide (and also the protoxide) of chromium, ignited with an alkaline carbonate, or better with a mixture of the carbonate and nitre, is converted into chromic acid, which unites with the alkali ; and on dissolving the fused product in water, filtering if necessary, and neutralising with acetic acid, the characteristic reactions of chromic acid (p. 164.)

* H. Loewel, Ann. Ch. Phys. [3.] xl. 42.

may be obtained with lead and silver-salts. An oxide of chromium fused with borax, in either blowpipe flame, yields an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart decided colours to the bead.

A *sesquisulphide of chromium*, Cr_2S_3, corresponding with the oxide, is obtained by exposing the latter, in a porcelain tube, to the vapour of bisulphide of carbon, at a bright red heat. It is a substance of a dark grey colour, which is dissolved by nitric acid.

Sesquichloride of chromium, Chromic chloride, Cr_2Cl_3; 160·1 or 2001·2.—This salt is obtained as a sublimate of a peach-purple colour, when chlorine is passed over a mixture of oxide of chromium and charcoal, ignited in a porcelain tube: or in the hydrated state by evaporating the solution of sesquichloride of chromium to dryness. The salt obtained by the latter process is a green powder containing $Cr_2Cl_3 + 9HO$. When heated, it gives off water and hydrochloric acid, and leaves a residue of oxychloride of chromium. Heated in a current of hydrochloric acid gas, it likewise parts with its water, and is converted into the violet anhydrous sesquichloride. The solution, evaporated in vacuo, leaves an amorphous mass which dissolves in water with evolution of heat, and consists of $Cr_2Cl_3 + 6HO$ (Péligot). Anhydrous sesquichloride of chromium is perfectly insoluble in cold water, and dissolves but very slowly in boiling water; but if to cold water in which the sesquichloride is immersed, there be added a very small quantity, even $\frac{1}{10000}$, of protochloride of chromium, a green solution is formed identical with that which is obtained by dissolving chromic oxide in hydrochloric acid (Péligot).

Chromic sulphate, $Cr_2O_3.3SO_3$; 197·6 or 247·0.—Chromic oxide is dissolved by sulphuric acid, but the salt does not crystallise. Chromic sulphate exhibits a violet and a green modification. The violet sulphate is obtained by leaving 8 parts of hydrated chromic oxide, dried at 212°, and 8 or 10

parts of strong sulphuric acid in a loosely stoppered bottle for several weeks. The solution, which is green at first, gradually becomes blue, and deposits a greenish blue crystalline mass. On dissolving this substance in water, and adding alcohol, a violet-blue crystalline precipitate is formed; and by dissolving this precipitate in very weak alcohol, and leaving the solution to itself for some time, small regular octahedrons are deposited, containing $Cr_2O_3 . 3SO_3 + 15HO$. The *green sulphate* is prepared by dissolving chromic oxide in strong sulphuric acid at a temperature between 122° and 140°; also by boiling a solution of the violet sulphate. The liquid, when quickly evaporated, yields a green crystalline salt, having the same composition as the violet sulphate. The green sulphate dissolves readily in alcohol, forming a blue solution; but the violet salt is insoluble in alcohol. The solution of the green sulphate is not completely decomposed by soluble baryta-salts at ordinary temperatures, a boiling heat being required to complete it; the violet sulphate, on the contrary, is deprived of all its sulphuric acid by baryta-salts at ordinary temperatures. When either the green or the violet sulphate is heated to 390°, with excess of sulphuric acid, a light yellow mass is obtained, which, when further heated, leaves a residue of anhydrous chromic sulphate, having a *red* colour. This anhydrous salt is completely insoluble in water, and dissolves with difficulty even in acid liquids.*

Chromic sulphate forms a crystallisable double salt with sulphate of potash, viz., *chrome-alum*, $KO . SO_3 + Cr_2O_3 . 3SO_3 + 24HO$. This salt is produced when a mixture of its constituent salts, with a little free sulphuric acid, is left to spontaneous evaporation. The best mode of preparing it is to mix three parts of a saturated solution of neutral chromate of potash, first with one part of oil of vitriol, and then with two parts of alcohol, which is to be added by small portions to the

* Regnault, Cours de Chimie.

mixture of acid and chromate, and not to apply artificial heat. The chromic acid is thus deoxidised in a gradual manner, and large crystals of the double sulphate are slowly deposited (Fischer). The octohedral crystals of chrome-alum are of a dark purple colour, and of a beautiful ruby-red, when so small as to be transparent. The solution is bluish-purple, but when heated to 140° or 180° becomes green, and, according to Fischer, either deposits on evaporation a bright-green amorphous, difficultly soluble mass, or yields crystals of sulphate of potash, while green chromic sulphate remains in solution. According to Loewel*, on the contrary, the change of the purple into the green salt does not arise from a separation of the two simple salts, but merely from loss of water of crystallisation. A solution of chrome-alum, which has become green and uncrystallisable by heating, does not deposit any sulphate of potash even when concentrated; neither does that salt separate when the crystals are melted in a sealed tube; but the green liquid obtained by either of these processes yields, when heated to 77° and 86° in a dry atmosphere, a dark green mass containing $Cr_2O_3.3SO_3 + KO.SO_3$, with scarcely 6 eq. water (Loewel). The violet crystals containing 24 Aq., when left for several days in dry air at a temperature between 77° and 86°, give off 12 Aq., and assume a lilac colour. At 212°, another quantity of water goes off, and the crystals become green; and, by gradually raising the temperature to about 660°, the whole of the water may be expelled without causing the salt to melt. The anhydrous crystals are green, and dissolve without residue in boiling water, but at a temperature somewhat above 660°, they suddenly become greenish-yellow, without perceptible loss of weight, and are afterwards perfectly insoluble in water.

Oxalate of chromium and potash, $3(KO.C_2O_3) + Cr_2O_3.3C_2O_3 + 6HO$. — This is another beautiful double salt of chromium.

* Ann. Ch. Phys. [3.] xliv. 313.

It is easily prepared by the following process of Dr. Gregory:—One part of bichromate of potash, two parts of binoxalate of potash, and two parts of crystallised oxalic acid are dissolved together in hot water. A copious evolution of carbonic acid gas takes place, arising from the deoxidation of the chromic acid, at the expense of a portion of the oxalic acid; and nothing fixed remains, except the salt in question, of which a pretty concentrated solution crystallises upon cooling in prismatic crystals, which are black by reflected light, but of a splendid blue by transmitted light, when sufficiently thin to be translucent. The oxide of chromium is not completely precipitated from this salt by an alkaline carbonate; and it is remarkable that only a small portion of the oxalic acid is thrown down from it by chloride of calcium. When fully dried and then carefully ignited, this salt is completely decomposed, and leaves a mixture of chromate and carbonate of potash. The corresponding double oxalate of chromium and soda contains 9HO, according to Mitscherlich. In the analogous oxalate of ferric oxide and soda, the proportion of water appeared to the author to be 10HO.

The mineral *chrome-iron*, $FeO.Cr_2O_3$, crystallises in octohedrons, and corresponds with the magnetic oxide of iron, having the sesquioxide of iron replaced by sesquioxide of chromium. Its density is 4·5; it is about as soft as felspar, and infusible. When exposed to long-continued calcination, in contact with carbonate of potash, in a reverberatory furnace, the oxide of chromium of this compound absorbs oxygen, and combines as chromic acid with the potash, while the protoxide of iron becomes sesquioxide. The addition of nitre increases the rapidity of oxidation, but is not absolutely required in the process. A yellow alkaline solution of carbonate and chromate of potash is obtained by lixiviating the calcined matter, which is generally converted into the red chromate or bichromate of potash, by the addition of the proper quantity of sulphuric acid, the latter salt being

more easily purified by crystallisation than the neutral chromate.

Chromic acid, CrO_3, 52·19 *or* 651·8.—This acid is not liberated from the chromates in a state of purity by any acid except the fluosilicic; it is also easily altered. Fluosilicic acid gas is conducted into a warm solution of bichromate of potash, till the potash is completely separated as the insoluble fluoride of silicon and potassium, which may be ascertained by testing a few drops of the solution with tartaric acid or chloride of platinum. The solution is evaporated to dryness by a steam heat, and the chromic acid redissolved by water; it gives an opaque, dull red solution. Chromic acid may also be obtained anhydrous and in acicular crystals, by distilling, in a platinum retort, a mixture of 4 parts of chromate of lead, 3 parts of finely pulverised fluor spar, and 7 parts of Nordhausen sulphuric acid; sulphate of lime is formed, together with perfluoride of chromium, the vapour of which is received in a large platinum crucible, covered with wet paper and used as a condenser. The perfluoride is decomposed by the aqueous vapour from the paper, being resolved into hydrofluoric acid and beautiful orange-red acicular crystals of chromic acid, which fill the crucible. A third and easier method of preparing chromic acid is to mix a solution of bichromate of potash, saturated between 122° and 140°, with $1\frac{1}{2}$ times its volume of strong sulphuric acid, adding the acid by successive small portions. Bisulphate of potash is then formed, which remains in solution, and the liquid, as it cools, deposits the chromic acid in long red needles. These may be drained, first in a funnel, afterwards on a brick; then dissolved in water; the solution treated with a small quantity of chromate of baryta to remove the last portion of sulphuric acid; and the filtered liquid evaporated in vacuo. Chromic acid differs remarkably from sulphuric acid, in having but little affinity for basic water, so that it may be obtained anhydrous by evaporating its solution to dryness. Indeed, the chromate of

water is not known to exist, even in combination, both the bichromate and terchromate of potash being anhydrous salts. The free acid is a powerful oxidizing agent, and bleaches organic colouring matters: chromic acid then loses half its oxygen, and becomes oxide of chromium. It is also converted into sesquichloride of chromium by hydrochloric acid, with evolution of chlorine:

$$2CrO_3 + 6HCl = Cr_2Cl_3 + 6HO + 3Cl;$$

and into sesquioxide by hydrosulphuric acid, with precipitation of sulphur:

$$2CrO_3 + 3HS = Cr_2O_3 + 3HO + 3S.$$

Sulphurous acid passed through a solution of chromic acid, or its salts, throws down a brown precipitate, consisting of monochromate of chromic oxide, or bioxide of chromium; $Cr_2O_3 . CrO_3 = 3CrO_2$. The other intermediate oxides, or chromates of chromic oxide mentioned on page 153., are formed by other imperfect reductions of chromic acid, or by the imperfect oxidation of chromic oxide. They are all brown substances, soluble in potash and in nitric acid. One of them, the bichromate, dissolves also without decomposition in hydrochloric and sulphuric acid; the others are reduced by hydrochloric acid to sesquichloride, with evolution of chlorine, and resolved by sulphuric acid into chromic acid and sulphate of chromic oxide.*

Chromic acid forms bibasic, monobasic, biacid, and a few tri-acid salts. The monochromates of the alkalies are yellow, the bichromates red; the chromates of the metals proper are bright yellow, red, or occasionally of some other colour. All chromates heated with oil of vitriol give off oxygen, and form sulphate of chromic oxide, together with another sulphate. When heated with hydrochloric acid, they give off chlorine

* For a full account of these brown oxides, see the translation of Gmelin's Handbook, iv. 113.

and form sesquichloride of chromium, together with another metallic chloride. Heated in the anhydrous state with common salt and sulphuric acid, they give off red vapours of chlorochromic acid, which condense to a brownish red liquid. Similarly, when heated with fluor spar and sulphuric acid, they give off red vapours of terfluoride of chromium. A few only of the chromates, more particularly those of the alkalies, are soluble in water, but they all dissolve in nitric acid. Solutions of the alkaline chromates form a pale yellow precipitate with baryta salts; bright yellow with lead-salts; brick red with mercurous salts; and crimson with silver salts.

Chromate of potash, Yellow chromate of potash, $KO.CrO_3$; 97·8 or 1222·5.—This salt is produced in the treatment of the chrome ore, but is seldom crystallised. It may be formed from the bichromate, by fusing that salt with an equivalent quantity of carbonate of potash; or by adding caustic potash to a red solution of the bichromate, till its colour becomes a pure golden yellow. The solution of chromate of potash has a great tendency to effloresce upon the sides of the basin when evaporated. Its crystals are of a yellow colour, anhydrous, and isomorphous with sulphate of potash. One hundred parts of water at 10° dissolve $48\frac{1}{3}$ parts of this salt; the solution preserves its yellow colour, even when diluted to a great degree.

Bichromate of potash, Red chromate of potash.—$KO.2CrO_3$; 148·6 or 1857·5.—This beautiful salt, of which a large quantity is consumed in the arts, crystallises in prisms or in large four-sided tables, of a fine orange-red colour. It fuses below a red heat, and forms on cooling a crystalline mass, the crystals of which have, according to Mitscherlich, the same form as those obtained from an aqueous solution; but this mass falls to powder as it cools, from the unequal contraction of the crystals in different directions. At 60°, water dissolves $\frac{1}{10}$ of its weight of this salt, and at the boiling point a considerably greater quantity.

Bichromate of chloride of potassium, Péligot's salt, $KCl.2CrO_3$.—This salt, which we are obliged to designate as if it contained chloride of potassium combined as a base with chromic acid, is formed by dissolving together, with the aid of heat, about three parts of bichromate of potash and four of concentrated hydrochloric acid, with a small quantity of water, avoiding the evolution of chlorine. It crystallises in flat red quadrangular prisms, and is decomposed by solution in pure water.

Terchromate of potash, $KO.3CrO_3$, is obtained crystallised when a solution of the bichromate is mixed with nitric acid, and evaporated. Bichromates of soda and silver exist which are anhydrous, like the bichromate of potash (Warington).

Chromate of soda, $NaO.CrO_3+10HO$.—By the evaporation of a concentrated solution of this salt, it is obtained in large fine crystals, having the form of glauber salt. The bichromate crystallises in thin, hyacinth-red, six-sided prisms, bevelled at the ends.

Chromate of ammonia, $NH_4O.CrO_3$ is prepared by evaporating a mixture of chromic acid with a slight excess of ammonia. It crystallises in lemon-yellow needles, very soluble in water, and having an alkaline reaction and pungent saline taste. When heated, they give off ammonia, water, and oxygen, and leave sesquioxide of chromium. The *bichromate*, $NH_4O.2CrO_3$, forms orange-yellow or reddish brown rhombic tables, which at a heat below redness are decomposed, with emission of light and feeble detonation, leaving the sesquioxide. It combines with chloride of mercury, forming crystalline compounds, containing $NH_4O.2CrO_3.HgCl+HO$, and $3(NH_4O.2CrO_3).HgCl$ (Richmond and Abel).* Rammelsberg has obtained an acid salt composed of $NH_4O.6CrO_3+10HO$.

Chromate of baryta, $BaO.CrO_3$ is a lemon-yellow powder obtained by precipitating a baryta-salt with an alkaline chromate.

* Chem. Soc. Qu. J. iii 139.

It is insoluble in water, but dissolves easily in nitric, hydrochloric, or chromic acid. When a baryta-salt is precipitated with neutral chromate of potash, and sulphuric acid added, the precipitate dissolves with partial decomposition, and on diluting with water, mixing the filtered solution with chromic acid, and evaporating in vacuo, neutral chromate of baryta first separates, then crystals of a *bichromate*, $BaO.2CrO_3+2HO$, and afterwards a double salt containing $2(BaO.3CrO_3.HO)+(KO.3CrO_3.HO)$. (Bahr.)*

Neutral chromate of lime, $CaO.CrO_3$, is obtained by treating carbonate of lime with aqueous chromic acid; and by treating the neutral salt with excess of chromic acid and evaporating, a *bichromate*, $CrO.2CrO_3 + 2HO$, is obtained. Chloride of calcium mixed with monochromate of potash, yields a double salt containing $5(CaO.CrO_3)+KO.CrO_3$. (Bahr.)

Chromate of magnesia forms, according to the author's observations, yellow crystals which are very soluble, and contain 5HO. It does not form a double salt with chromate of potash, as sulphate of magnesia does with sulphate of potash. It is remarked that the insoluble metallic chromates generally carry down portions of the neutral precipitating salts, or of subsalts, and their analysis is often unsatisfactory from that cause. When the magnesian chromates are compared with the sulphates of the same family, the former are found to have their water readily replaced by metallic oxides, but not by salts; so that subchromates with excess of oxide are numerous, while few or no double chromates exist.

Chromate of lead, $PbO.CrO_3$; 162·4 or 2030.—This compound, so well known as *chrome-yellow*, is obtained by mixing nitrate or acetate of lead with chromate or bichromate of potash. The precipitate is of a lighter shade from dilute than from concentrated solutions. It is entirely soluble in potash or soda, but not in dilute acids.

Subchromate of lead, $2PbO.CrO_3$, is of a red colour. It is

* J. pr. Chem. lx. 60.

formed when a solution of neutral chromate of potash, mixed with as much free alkali as it already contains, is added to a solution of nitrate of lead. But the finest vermilion-red subchromate is formed when one part of the neutral chromate of lead is thrown into five parts of nitre in a state of fusion by heat. Water dissolves the chromate and nitrate of potash in the fused mass, and leaves the subchromate of lead as a crystalline powder, (Liebig and Wöhler). An orange pigment may be obtained very economically, by boiling the sulphate of lead, which is a waste product in making acetate of alumina from alum by means of acetate of lead, with a solution of chromate of potash. The subchromate of lead forms a beautiful orange upon cloth, which is even more stable than the yellow chromate, not being acted upon by either alkalies or acids. One method of dyeing chrome-orange, is to fix the yellow chromate of lead first in the calico, by dipping it successively in acetate of lead and bichromate of potash, and then washing it. This should be repeated, in order to precipitate a considerable quantity of the chromate in the calico. A milk of lime is then heated in an open pan; and when it is at the point of ebullition, the yellow calico is immersed in it, and instantly becomes orange, being deprived of a portion of its chromic acid by the lime, which forms a soluble chromate of lime. At a lower temperature, lime-water dissolves the chromate of lead entirely, and leaves the cloth white.

Chromate of silver falls as a reddish brown precipitate when nitrate of silver is added to neutral chromate of potash. Dissolved in hot and concentrated solution of ammonia, it yields, on cooling, large well formed crystals, $AgO\,CrO_3 + 2NH_3$, isomorphous with the analogous ammoniacal sulphate and seleniate of silver.

Chlorochromic acid, CrO_2Cl, or $2CrO_3.CrCl_3$.—This is a volatile liquid, obtained by distilling, in a glass retort, at a gentle heat, 3 parts of bichromate of potash and $3\frac{1}{2}$ parts of common salt, previously reduced to powder and mixed

together, with 5 parts by water-measure of oil of vitriol, discontinuing the distillation when the vapours, from being of a deep orange-red, become pale — that change arising from watery vapour. The compound is a heavy red liquid, decomposed by water. The density of its vapour is 5·9.

Terfluoride of chromium, CrF_3, is obtained in the manner already mentioned under the preparation of chromic acid. It is a blood-red liquid. No corresponding terchloride of chromium has been obtained in an isolated state.

Perchromic acid, Cr_2O_7. — When peroxide of hydrogen dissolved in water is mixed with a solution of chromic acid, the liquid assumes a deep indigo-blue colour, but often loses this colour very rapidly, giving off oxygen at the same time. The same blue colour is formed by adding a mixture of aqueous peroxide of hydrogen and sulphuric or hydrochloric acid to bichromate of potash; but, in a very short time, oxygen is evolved, and a potash-salt, together with a chromic salt, left in solution. For each atom of $KO.2CrO_3$, four atoms of oxygen are evolved, provided an excess of HO_2 be present:

$$KO.2CrO_3 + O + 4SO_3 = KO.SO_3 + Cr_2O_3.3SO_3 + 4O.$$

The peroxide of hydrogen first gives up 1 at. O to the 2 at. of CrO_3, and forms Cr_2O_7; and this compound is subsequently resolved into Cr_2O_3 and 4O. With ether, perchromic acid forms a more stable blue mixture than with water, and in this state may be made to unite with ammonia and with certain organic bases, forming very stable compounds, from which stronger acids separate the blue acid.

ESTIMATION OF CHROMIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Chromium is usually estimated in the state of sesquioxide. When it exists in solution in that state, it may be precipitated

by ammonia, care being taken to avoid a large excess of that reagent (which would dissolve a portion), and to heat the liquid for some time. The chromic oxide is then completely precipitated, and the precipitate, after washing and drying, is reduced by ignition to the state of anhydrous sesquioxide, containing 70·1 per cent. of the metal.

When chromium exists in solution in the state of chromic acid, it is best to precipitate it by a solution of mercurous nitrate; the mercurous chromate thereby thrown down yields by ignition the anhydrous sesquioxide. The chromic acid might also be precipitated and estimated in the form of a baryta or lead salt.

Chromic acid may also be estimated by means of oxalic acid, which reduces it to sesquioxide, being itself converted into carbonic acid. The quantity of carbonic acid evolved determines the quantity of chromic acid present, 3 eq. CO_2 corresponding to 1 eq. CrO_3, as shown by the equation:

$$2CrO_3 + 3C_2O_3 = Cr_2O_3 + 6CO_2.$$

The mode of proceeding is the same as that adopted for the valuation of black oxide of manganese (p. 17). If the object be merely to determine the quantity of chromium present, any salt of oxalic acid may be used; but if the alkalies are also to be estimated in the remaining liquid, the ammonia or baryta salt must be used.

Chromic oxide, in the state of neutral or acid solution, is easily separated from the *alkalies* or *alkaline earths*, by precipitation with ammonia, care being taken in the latter case to protect the liquid and precipitate from the air. The same method, with addition of sal-ammoniac, serves to separate chromic oxide from *magnesia*. The separation from the alkaline earths and from magnesia may also be effected by precipitating the whole with an alkaline carbonate, and igniting the precipitate with a mixture of carbonate of soda and nitre. The chromium is then converted into chromate of soda, which

may be dissolved out, and the solution, after neutralisation with nitric or acetic acid, treated with mercurous nitrate as above.

From *alumina* and *glucina*, chromic oxide may be separated by treating the solution with excess of potash, and boiling the liquid to precipitate the chromic oxide. The separation is, however, more completely effected by fusing with nitre and carbonate of soda, treating the fused mass with water, adding an excess of nitric acid to dissolve anything that may be insoluble in water, and precipitating the alumina or glucina by ammonia.

Another method of converting chromic oxide into chromic acid, and thereby effecting its separation from the above-mentioned oxides, is to treat the mixture with excess of potash, and heat the solution gently with bioxide of lead. The whole of the chromium is then converted into chromic acid, and remains dissolved as chromate of lead in the alkaline liquid; and on filtering from the excess of bioxide of lead, and any other insoluble matter that may be present, and supersaturating the filtrate with acetic acid, the chromate of lead is precipitated (Chancel).*

Chromic acid may be separated from the alkalies in neutral solutions by precipitation with mercurous nitrate; also by reducing it to chromic oxide with hydrochloric acid and alcohol, and precipitating by ammonia. From the *earths* it may also be separated by this latter method, or, again, by fusing with carbonate of soda, dissolving out with water, &c.

From *manganese*, *iron* (in the state of protoxide), *cobalt*, *nickel*, and *zinc*, chromium in the state of sesquioxide may be separated by agitation with carbonate of baryta, which precipitates the chromic oxide, leaving the protoxides in solution. The precipitate is then treated with dilute sulphuric acid, which dissolves the chromic oxide and leaves the baryta,

* Compt. rend. xliii. 927.

and the filtrate treated with ammonia to precipitate the chromic oxide. Chromium may also be separated from all these metals, except manganese, by fusion with nitre and carbonate of soda, or with the carbonate alone if it is already in the form of chromic acid. Or, again, the separation may be effected by means of potash and bioxide of lead, according to Chancel's method above described.

From *cadmium, copper, lead,* and *tin,* chromium is easily separated by hydrosulphuric acid.

When sesquioxide of chromium and chromic acid occur together in a solution, the chromic acid may be precipitated by mercurous nitrate, the solution being first completely neutralised, and the sesquioxide precipitated from the filtrate by ammonia, which at the same time throws down a mercury-compound, to be afterwards separated from the chromic acid by ignition.

SECTION IV.

VANADIUM.

Eq. 68·55 *or* 856·9; V.

Vanadium, so named from *Vanadis,* a Scandinavian deity, was discovered by Sefstrœm in 1830, in the iron prepared from the iron ore of Taberg, in Sweden, and procured afterwards in larger quantity from the slag of that ore. It was found afterwards by Mr. Johnston, in a new mineral discovered by him, the vanadiate of lead, from Wanlockhead. It is one of the rarest of the elements. The metal itself has considerable resemblance in properties to chromium. It combines with oxygen in three proportions, forming the protoxide of vanadium, VO, bioxide, VO_2, and vanadic acid, VO_3.

Protoxide of vanadium, VO, 76·55 *or* 956·9, is produced by the action of charcoal or hydrogen upon vanadic acid. It is a black powder of semi-metallic lustre, and when made coherent by pressure, conducts electricity like a metal. It does not combine with acids, and exhibits none of the characters of an alkaline base. It is readily oxidised when heated in the open air, and passes into the following compound.

Bioxide of vanadium, Vanadic oxide, VO_2, 84·55 *or* 1056·9, is produced by the action of hydrosulphuric acid and other deoxidating substances upon vanadic acid. When pure, it is a black pulverulent substance, quite free from any acid or alkaline reaction. It dissolves in acids, and forms salts, most of which are of a blue colour. Vanadic salts form, with the *hydrates* and *monocarbonates* of the *fixed alkalies*, a greyish-white precipitate of hydrated vanadic oxide, which dissolves in a moderate excess of the reagent, but is precipitated by a large excess in the form of a vanadite of the alkali. *Ammonia* in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia. *Ferrocyanide of potassium* forms a yellow precipitate, which turns green on exposure to the air. *Hydrosulphuric acid* produces no precipitate. *Sulphide of ammonium* forms a black-brown precipitate, soluble in excess. *Tincture of galls* forms a finely-divided black precipitate, which gives to the liquid the appearance of ink.

Bioxide of vanadium is also capable of acting as an acid, and forms compounds with alkaline bases, some of which are crystallisable. It is hence called *vanadous acid*, and its salts *vanadites*. These salts in the dry state are brown or black; they are all insoluble in water, excepting those of the alkalies. The solutions of the alkaline vanadites are brown, but when treated with hydrosulphuric acid, they acquire a splendid red-purple colour, arising from the formation of a sulphur-salt. Acids colour them blue, by forming a double salt of vanadic

oxide and the alkali. Tincture of galls colours them blackish-blue. The insoluble vanadites, when moistened or covered with water, become green, and are converted into salts of vanadic acid.

Vanadic acid, VO_3; 92·55 *or* 1156·9.—It is in this state that vanadium occurs in the slag of the iron-ore of Taberg, and in the vanadiate of lead. It is obtained by dissolving the latter mineral in nitric acid, and precipitating the lead and arsenic, with which the vanadium is accompanied, by hydrosulphuric acid. A blue solution of bioxide of vanadium remains, which becomes vanadic acid when evaporated to dryness. Vanadic acid fuses but retains its oxygen at a strong red heat. It is very sparingly soluble, water taking up only 1-100th of its weight of this compound, thereby acquiring a yellow colour and an acid reaction. It acts the part of a base to stronger acids. An interesting double phosphate of silica and vanadic acid was observed in crystalline seales, of which the formula is $2SiO_3.PO_5 + 2VO_3.PO_5 + 6HO$. Vanadie acid forms, with bases, neutral and acid salts, the first of which admit of an isomeric modification, being both white and yellow, while the acid salts are of a fine orange-red. Vanadic and chromic acids are the only acids of whieh the solution is red, while they are distinguished from each other by the vanadic acid becoming blue, and the chromic acid green, when they are deoxidised. All the vanadiates are, more or less soluble in water; some of them, however, as the baryta and lead salts, are very sparingly soluble. The vanadiates of the alkalies are sparingly soluble in cold water, especially if it contains a free alkali or another alkaline salt; *e. g.*, vanadiate of ammonia is nearly insoluble in water eontaining sal-ammoniac; hence on treating a solution of vanadiate of potash with excess of sal-ammoniac, a precipitate of vanadiate of ammonia is produced. The aqueous solutions of the vanadiates are coloured red by the stronger acids, but the mixture often becomes colourless again after a while. They

give orange-red precipitates with the salts of *teroxide of antimony, protoxide of lead, protoxide of copper,* and *protoxide of mercury. Hydrosulphuric acid* produces in neutral solutions of the vanadiates a mixed precipitate of sulphur and hydrated vanadic oxide; in acid solutions, it merely throws down sulphur and reduces the vanadic acid to vanadic oxide. *Sulphide of ammonium* imparts to solutions of the vanadiates a brown-red colour, and, on adding an acid to the solution, a light brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur; the liquid at the same time generally acquires a blue colour.

All compounds of vanadium heated with *borax* or *phosphorus salt* in the outer blowpipe flame, produce a clear bead, which is colourless if the quantity of vanadium be small, yellow if it be large; in the inner flame, the bead acquires a beautiful green colour.

Sulphides and chlorides of vanadium, corresponding with the bioxide and vanadic acid have likewise been formed.*

ESTIMATION OF VANADIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Vanadium, in the state of vanadic oxide or vanadic acid, is estimated by reducing it to the state of protoxide by ignition in a stream of hydrogen; 100 parts of the protoxide contain 90·54 of the metal.

In solutions of vanadous salts, the vanadium is precipitated by mixing the solution with excess of mercuric chloride (corrosive sublimate), and then with ammonia. The precipitate, consisting of mercuric vanadiate, and amido-chloride of mercury, is ignited, whereupon vanadic acid remains mixed only with a small quantity of mercuric oxide, from which it is separated by solution in carbonate of ammonia.

* Berzelius, Ann. Ch. Phys. [2.] xlvii. 337.

When vanadic acid is dissolved in a liquid, it may be obtained by evaporating the liquid, and if volatile acids or ammonia are also present, by igniting the residue.

Vanadic acid may be separated from many acids and other substances, by causing it to unite with ammonia, expelling the excess of ammonia by evaporation, and then adding a saturated solution of sal-ammoniac, in which vanadiate of ammonia is insoluble. The precipitate is then washed on a filter, first with solution of sal-ammoniac, then with alcohol, and the ammonia driven off by ignition. This method serves to separate vanadic acid from the fixed alkalies.

Vanadium may be separated from many of the preceding metals by the solubility of its sulphide in sulphide of ammonium; and from others, which are precipitated from their acid solutions by hydrosulphuric acid, by acidulating the liquid, and passing hydrosulphuric acid gas through it; the vanadium then remains dissolved in the form of vanadic oxide.

From *lead*, *baryta*, and *strontia*, vanadic acid may be separated by fusion with bisulphate of potash; on treating the fused mass with water, sulphate of lead, baryta, or strontia remains, while vanadiate of potash is dissolved. Sulphuric acid cannot be used to effect this separation, because the precipitated sulphate always carries down with it a portion of the vanadium.

SECTION V.

TUNGSTEN.

Syn. WOLFRAM. *Eq.* 94·64, *or* 1183; W.

This element exists in the form of tungstic acid in several minerals, the most important of which are the native *tungstate of lime* $CaO.WO_3$, and *wolfram*, or the tungstate of manganese and iron, $MnO.WO_3+3(FeO.WO_3)$. Its name tungsten

means in Swedish, *heavy stone*, and is expressive of the great density of its compounds.

Tungstic acid parts with oxygen easily, and may be reduced in a glass tube, by means of dry hydrogen gas, at a red heat. The metal is thus obtained in the state of a dense, dark grey powder, which it is necessary to expose to a very violent heat to fuse into globules, for tungsten is even less fusible than manganese. The metal, when fused, has the colour and lustre of iron, and is not altered in air: it is one of the densest of the metals, its specific gravity being from 17·22 to 17·6. By passing the vapour of chloride or oxychloride of tungsten mixed with hydrogen, through a red-hot glass tube, the metal is obtained in the form of a dense specular film of steel-grey colour, and sp. gr. 16·54 (Wöhler). When heated to redness in the pulverulent form, it takes fire, burns, and is converted into tungstic acid. Tungsten forms two compounds with oxygen, viz., tungstic oxide, WO_2, and tungstic acid, WO_3.

Tungstic oxide, WO_2, 110·64 or 1383.—This oxide is obtained as a brown powder when tungstic acid is reduced by hydrogen at a temperature not exceeding low redness. Tungstic acid may also be deprived of oxygen in the humid way, by pouring diluted hydrochloric acid over it, and placing zinc in the liquor; the tungstic acid then gradually changes into tungstic oxide, in the form of brilliant crystalline plates of a copper-red colour. No saline compounds of this oxide with acids are known. When digested in a strong solution of hydrate of potash, it dissolves, with disengagement of hydrogen gas and formation of tungstate of potash.

A compound of tungstic oxide and soda, $NaO.2WO_2$, of a very singular nature, was discovered by Wöhler. It is obtained by adding to fused tungstate of soda as much tungstic acid as it will take up, and exposing the mass at a red heat to hydrogen gas. After dissolving out the neutral undecomposed tungstate by water, the new compound remains in golden

yellow scales and regular cubes, possessing the metallic lustre of, and a striking resemblance to gold. This compound is not decomposed by aqua regia, sulphuric or nitric acid, or by alkaline solutions, but yields to hydrofluoric acid. It cannot be prepared by uniting soda directly with tungstic oxide.

Tungstic acid, WO_3; 118·64 or 1483, is most conveniently obtained by decomposing the native tungstate of lime, finely pulverised, by hydrochloric acid; chloride of calcium is dissolved, and tungstic acid precipitates. It is also obtained from wolfram by digesting that mineral in nitro-hydrochloric acid, which dissolves the oxides of iron and manganese, and leaves the tungstic acid in the form of a yellow powder—or by fusing the mineral with four times its weight of nitre; treating the fused mass with water to dissolve out the tungstate of potash thereby produced; adding chloride of calcium to the filtrate to throw down the tungstic acid as tungstate of lime; and decomposing the washed lime-salt with nitric acid. Dissolved in ammonia and reprecipitated by acids, tungstic acid always forms a compound with the acid employed. It may be obtained in the separate state by heating the tungstate of ammonia to redness. It is an orange-yellow powder, which becomes dull green when strongly heated. Its density is 6·12. It is quite insoluble in water and in acids, but dissolves in alkaline solutions.

Tungstic acid forms both neutral and acid salts with the alkalies. Neutral *tungstate of potash* $KO.WO_3$ is a very soluble salt, which may be obtained in small crystals by evaporating its solution. When a little acid is added to the solution, an acid salt precipitates, which is very slightly soluble in water. The neutral *tungstate of soda* is also very soluble, but may be obtained in good crystals, which contain a large quantity of water of crystallisation. The acid tungstate of soda $NaO.2WO_3$ is very crystallisable, and soluble in eight parts of water. A combination of tungstic acid with tungstic oxide, $WO_2.WO_3$, is obtained as a fine blue powder when tungstate of ammonia is heated to redness in a

retort, and is also produced under other circumstances. Malaguti is disposed to consider this compound as a distinct acid of tungsten, W_2O_5.*

All the salts of tungstic acid have a very high specific gravity. The alkaline and earthy tungstates are colourless. The only soluble tungstates are those of the alkalies and magnesia. Solutions of the alkaline tungstates give, with hydrochloric, nitric, sulphuric, and phosphoric acid, white precipitates consisting of compounds of tungstic acid with the other acid. The precipitate formed by phosphoric acid dissolves in excess of that reagent; the precipitates formed by the other three acids turn yellow on boiling. A solution of an alkaline tungstate supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yields, on the introduction of a piece of zinc, a beautiful blue colour arising from the formation of blue oxide of tungsten; this effect is not produced with nitric, tartaric, or citric acid. Solutions of alkaline tungstates form with lime-water and with salts of baryta, lime, zinc, lead, mercury, and silver, white precipitates consisting of tungstates of those bases. A soluble tungstate mixed with sulphide of ammonium and then with an acid in excess, yields a light brown precipitate of sulphide of tungsten, soluble in sulphide of ammonium.

With borax and phosphorus-salt in the outer blow-pipe flame, tungstic acid forms a colourless bead; in the inner flame it forms with borax, a yellow glass, if the quantity of tungsten present be somewhat considerable, but colourless with a smaller quantity. With phosphorus-salt in the inner flame it forms a glass of a pure blue colour, unless iron is also present, in which case the colour is blood-red; the addition of tin, however, renders it blue.

The above mentioned characters of tungstic acid, though general, are not invariable. Tungstic acid appears to be susceptible of certain modifications analogous to those of phosphoric acid, and depending upon the proportions in which it

* Ann. Ch. Phys. [2], lx. 271.

unites with water and other bases. In some of these modifications it is much more soluble than in others, and is not precipitated by nitric or hydrochloric acid.

Laurent distinguished five or six classes of tungstates, viz.,

1. *Ordinary tungstates*, WO_3MO, with or without water (M denoting a metal or hydrogen). To this class belong the neutral potash, soda, and baryta-salts, and most of the insoluble salts of tungstic acid. No acid salts of this class appear to exist. The solution of an ordinary tungstate dropped into excess of dilute nitric acid produces a gelatinous precipitate. The hydrated tungstic acid obtained by the action of aqua regia on wolfram belongs to this variety, its formula being $WO_3.HO$. 2. *Paratungstates*, $W_4O_{12}.2MO$, with or without water. To this class belong the salts commonly called bitungstates of potash, soda, ammonia, baryta, &c. They all, excepting the soda-salt, dissolve but sparingly in water. The solutions give no precipitate on the addition of very small quantities of nitric acid, or of very weak hydrochloric acid. They give precipitates with the ammoniacal solutions of nitrate of magnesia, zinc, and silver, which the ordinary tungstates do not. 3. *Metatungstates*, $W_3O_9.MO$, with or without water. The ammonia-salt of this variety is formed by boiling a solution of the paratungstate for several hours; the solution filtered when cold and then evaporated to a syrup, yields very soluble octohedrons. The solution is not precipitated by concentrated hydrochloric acid.—4. *Isotungstates*, $W_2O_6.MO$, with or without water. The ammonia-salt is formed by boiling metatungstate of ammonia with excess of ammonia; it is but slightly soluble in water. The acid, which may be separated from it by means of another acid, is principally characterised by reproducing the isotungstate when treated with ammonia. 5. *Polytungstates*, $W_6O_{18}.3MO$. When the yellow acid obtained from wolfram is treated with ammonia, and the solution slowly evaporated, paratungstate of ammonia is first deposited and afterwards the isotungstate. The mother-liquor separates

into two layers, one of which is brown and syrupy, and changes on drying to an easily soluble crystalline mass, probably a double salt of ammonia and iron. Boiled with strong nitric acid, it yields a precipitate which is not gelatinous, and does not turn yellow when boiled. Polystungstic acid is further characterised by forming with ammonia a very soluble salt, which becomes gummy on evaporation. 6. Laurent also, mentioned another class of tungstates, viz., *Homotungstates*, containing $W_5O_{15} . MO$. According to Margueritte * also there exist acid tungstates containing 3, 4, 5 and 6 eq. of acid to 1 eq. of base.

The composition of the tungstates has also been recently examined by W. Lotz †, whose results differ in many points from the preceding. According to Lotz, crude tungstic acid, obtained from wolfram by the action of hydrochloric and a small quantity of nitric acid, yields by digestion with ammonia and evaporation at a very gentle heat, yellow needles of an ammonia-salt containing $3NH_4O . 7WO_3 + 6HO$, or $2(NH_4O.2WO_3) + NH_4O . 3WO_3 + 6HO$. By mixing warm concentrated solutions of 1 eq. of monotungstate of soda, and rather more than 1 eq. chloride of ammonium, a double salt is obtained, composed of $(2NH_4O . WO_3) + NaO . WO_3 + 3HO$; and by adding 1 eq. metatungstate of soda to a boiling solution of 2 eq. chloride of ammonium, another double salt is formed containing $3NaO . 7WO_3 + 4(3NH_4O . 7WO_3) + 14HO$. The needle-shaped ammonia-salt mixed with solutions of the neutral salts of barium, strontium, manganese, nickel, and lead, yields precipitates of the general formula $3MO . 7WO_3$. With alumina a white curdy precipitate is formed containing $Al_2O_3 . 7WO_3 + 9HO$. Sesquioxide of chromium forms a salt of a similar constitution. With magnesia, a sparingly soluble crystalline double salt is formed, containing $2(MgO . 2WO_3) + NH_4O . 3WO_3 + 10HO$; a similar double salt with zinc. Cad-

* Ann. Ch. Phys. [3], xvii. 475.

† Ann. Ch. Pharm. xci. 49.

mium also forms a double salt containing $3NH_4O \cdot 7WO_3 + 4(3CdO \cdot 7W_3O) + 35HO$. To the octohedral tungstate of ammonia, which was regarded by Margueritte as $NH_4O \cdot 3WO_3 + 5HO$, and by Laurent as a metastungstate containing $(NH_4)_{\frac{5}{6}}H_{\frac{1}{6}}W_3O_{10} + 5HO$, or $\left.\begin{matrix} 5NH_4O \\ HO \end{matrix}\right\} 18WO_3 + 30HO$. Lotz assigns the formula $2(NH_4O \cdot 4WO_3) + 15$ eq. The solution of this salt is not precipitated by nitric or hydrochloric acid at ordinary temperatures, but after continued boiling yields a yellow precipitate; but if it be previously mixed with potash, the addition of an acid produces an immediate white precipitate, which turns yellow on boiling; the needle-shaped salt gives an immediate precipitate with acids, without previous addition of alkali. The octohedral salt differs from the needle-shaped salt also, in not forming precipitates with solutions of the earths and other metallic oxides, except when previously mixed with ammonia, by which, indeed, it is converted into the salt $3NH_4O \cdot 7WO_3$.

Sulphides of tungsten.—The bisulphide is prepared by mixing one part of tungsten with six parts of cinnabar, and exposing the mixture, covered with charcoal, in a crucible, to a white heat; or, according to Roche, by fusing bitungstate of potash with an equal weight of sulphur, and washing the fused mass with water. The tersulphide is formed by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid. It is of a liver-brown colour, and becomes black on drying. The tersulphide of tungsten has a certain degree of solubility in water containing no saline matter, and is a strong sulphur-acid. The salt $KS.WS_3$ forms pale red crystals. Two parts of this sulphur-salt dissolved in water with one part of nitre, give large and beautiful ruby-red crystals of a double salt, $KS.WS_3 + KO.NO_5$.

Phosphides of tungsten.—Phosphorus and tungsten combine directly, but without emission of light and heat, when finely pounded metallic tungsten contained in a glass tube is

heated to redness in phosphorus vapour. The resulting compound is a dull, dark grey powder, very difficult to oxidise, and containing W_3P_2. Another compound, W_4P, is obtained in magnificent crystalline groups, having exactly the appearance of natural geodes, by reducing a mixture of 2 eq. phosphoric and 1 eq. tungstic acids at a very high temperature in a crucible lined with charcoal. The crystals are six-sided prisms, sometimes an inch long, of a steel-grey colour, and strong lustre; their specific gravity is 5·207. This compound is a perfect conductor of electricity; undergoes no change when heated to the melting point of manganese in a close vessel, and remains nearly unaltered when heated to redness in the air; but burns with great splendour on charcoal in a stream of oxygen, or on fused chlorate of potash; it is not attacked by any acid, not even by aqua-regia (Wöhler).*

Bichloride of tungsten, WCl_2, is formed when metallic tungsten is heated in chlorine gas. It condenses in dark red needles, which are very fusible and volatile. This chloride is decomposed by water, and tungstic oxide with hydrochloric acid formed.

Terchloride of tungsten, WCl_3, is produced at the same time as the last compound, and also when the sulphide of tungsten is heated in chlorine gas. It forms a sublimate of beautiful red crystals, which are resolved by water into tungstic and hydrochloric acids. A *chlorotungstic acid*, or double compound of terchloride of tungsten and tungstic acid, WO_2Cl, or $WCl_3 . 2WO_3$, is prepared by heating tungstic oxide in chlorine gas. It condenses in yellow crystalline scales: when suddenly heated, it is resolved into tungstic acid, bichloride of tungsten, and chlorine. Another compound is known, containing $2WCl_3 . WO_3$ (Bonnet).

According to A. Riche†, the terchloride of tungsten is the only product obtained when tungsten is heated in pure dry

* Chem. Soc. Qu. J. v. 94.

† Compt. rend. xlii. 203.

chlorine gas: it crystallises in needles, not of a red but of a steel-grey colour. The bichloride is formed in small quantity, as a blackish-brown mass, by heating the terchloride in dry hydrogen; and the red oxychloride WCl_2O, by passing chlorine gas over a mixture of tungstic acid and charcoal, and distilling the product in an atmosphere of hydrogen.

ESTIMATION OF TUNGSTEN, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Tungsten is always estimated in the form of tungstic acid. When this acid exists in a solution not containing any other fixed substance, it is sufficient to evaporate to dryness and ignite the residue. The tungstic acid is then obtained in a state of purity, and contains 79·76 per cent. of the metal. Tungstic oxide is easily converted into tungstic acid by fusion with carbonate of soda.

The best method of separating tungstic acid from the *fixed alkalies* is to treat the solution, after exact neutralisation with nitric acid, with a solution of mercurous nitrate. Mercurous tungstate is then precipitated, and the mercury may be expelled from the dried precipitate by careful ignition in a good draught.

The separation of tungstic acid from the *earths* may be effected by decomposing the compound with nitric acid, and treating the decomposed mass with carbonate of ammonia, which dissolves the tungstic acid.

Tungstic acid may be readily separated from many metallic oxides, such as the oxides of *iron, manganese, nickel, cobalt, lead,* &c., by fusing the whole with carbonate of soda, and digesting the fused mass with water, which dissolves the tungstic acid and leaves the oxides undissolved.

From *titanic acid,* tungstic acid is separated by ammonia, which dissolves only the latter.

The best mode of separating tungstic acid from *chromic*

acid, is to treat the concentrated solution with excess of hydrochloric acid, which precipitates the greater part of the tungstic acid; then boil with alcohol to reduce the chromic acid to chromic oxide; and dissolve the tungstic acid by ammonia.

SECTION VI.

MOLYBDENUM.

Eq. 47·88 *or* 598·5; Mo.

This metal is closely allied to tungsten. Its native sulphide was first distinguished from plumbago by Scheele, in 1778; and a few years afterwards, molybdic acid, which he had formed, was reduced, and molybdenum obtained from it, by another Swedish chemist, Hjelm. The name molybdenum is derived from the Greek term for plumbago.

The oxides of molybdenum are easily reduced, when exposed to a strong heat in a crucible lined with charcoal, but the metal itself is very refractory. Bucholz, who obtained it in rounded buttons, found it to be a white metal, of density between 8·615 and 8·636. It may be reduced from its chlorides by hydrogen, like tungsten (p. 177.), and then forms a light steel-grey specular deposit, adhering to the glass (Wöhler). It is not acted upon by hydrochloric, hydrofluoric, or diluted sulphuric acid; but is dissolved by concentrated sulphuric acid, by nitric acid, and by aqua-regia. Hydrate of potash does not dissolve this metal in the humid way. Molybdenum combines in three proportions with oxygen, forming molybdous oxide, MoO, molybdic oxide, MoO_2, and molybdic acid, MoO_3.

Molybdous oxide, MoO, 55·88 *or* 698·5.—This oxide is obtained by adding to the concentrated solution of any

molybdate, so much hydrochloric acid as to redissolve the molybdic acid which is at first thrown down, and placing zinc in the liquid; this becomes first blue, then reddish-brown, and finally black, and contains the chloride of zinc and protochloride of molybdenum. To separate the oxide of molybdenum from the oxide of zinc, ammonia is added to the liquid in quantity no more than sufficient to precipitate the former, while the latter remains in solution. The molybdous oxide carries down with it a portion of oxide of zinc, from which it may be freed by washing with ammonia: it is thus obtained as a hydrate of a black colour. The hydrate of molybdous oxide dissolves with difficulty in acids, forming solutions which are almost black and opaque, and which do not yield crystallisable salts. These solutions yield with the *alkalies* and their *carbonates* a brownish-black precipitate of the hydrated oxide, insoluble in the caustic alkalies, slightly soluble in the neutral carbonates, but readily soluble in bicarbonate of potash or carbonate of ammonia. *Hydrosulphuric acid* throws down a brown-black precipitate, and *sulphide of ammonium* a yellowish-brown precipitate of sulphide of molybdenum, easily soluble in sulphide of ammonium. *Ferrocyanide* or *ferricyanide* of potassium forms a dark-brown precipitate, insoluble in excess. *Phosphate of soda* forms a brownish-white precipitate. Molybdous oxide resists, after ignition, the action of all acids.

Molybdic oxide, MoO_2; 63·88 *or* 798·5.—This oxide may be obtained by igniting molybdate of ammonia in a covered crucible, but mixed with a little molybdic acid. It is better procured by igniting rapidly, in a covered crucible, a mixture of anhydrous molybdate of soda (which may contain an excess of soda) with sal-ammoniac. Water poured upon the fused mass dissolves common salt, and leaves a brown powder almost black. But molybdic oxide prepared in this way is insoluble in acids. The hydrated oxide may

be obtained in various ways, one of which consists in digesting molybdic acid with hydrochloric acid and copper, till all the molybdic acid is dissolved. From the solution, which is of a deep-red colour, molybdic oxide is precipitated, in appearance exactly similar to the hydrated sesquioxide of iron, by ammonia added in sufficient excess to retain all the oxide of copper in solution. The hydrate has a certain degree of solubility in pure water, and should, therefore, be washed with solution of sal-ammoniac, and lastly with alcohol. This hydrate reddens litmus paper, but possesses no other property of an acid. It is not dissolved by the hydrated alkalies, but is soluble in their carbonates, like several earths and metallic oxides. It dissolves in acids and forms salts, which are red when they contain water of crystallisation, and black when anhydrous. The aqueous solutions of these salts have a reddish-brown colour, and a rough, somewhat acid and subsequently metallic taste. When heated in the air, they have a tendency to become blue by oxidation. With *zinc*, they first blacken, and then yield a black precipitate of hydrated molybdous oxide. Their behaviour with alkalies, hydrosulphuric acid &c., is similar to that of the molybdous salts, excepting that the precipitates are lighter in colour. The oxalate of molybdic oxide may be obtained in crystals by spontaneous evaporation.

Molybdic acid, MoO_3; 71·88 *or* 898·5.—The native sulphide of molybdenum, in fine powder, is roasted in an open crucible, with constant stirring, at a heat not exceeding low redness, so long as sulphurous acid goes off. It leaves a dull yellow powder, which is impure molybdic acid. This is dissolved in ammonia, and the molybdate of ammonia purified by evaporation, during which some foreign matters are deposited, and crystallised. The crystallised salt, exposed to a moderate heat, so as to avoid fusion, gives off its ammonia, and leaves molybdic acid in a state of purity. The acid thus prepared is

a white and light porous mass, which may be diffused in water, and divides into little crystalline scales of a silky lustre. It fuses at a red heat, and forms on cooling a straw-coloured crystalline mass, the density of which is 3·49. This acid forms no hydrate. It requires 570 times its weight of water to dissolve it. Before being ignited, it is soluble in acids, and forms a class of compounds, in which it appears to play the part of base, but of which not much is known. When boiled with bitartrate of potash, molybdic acid dissolves, even after being fused by heat.

When a solution of bichloride of molybdenum is poured into a saturated or nearly saturated solution of molybdate of ammonia, a blue precipitate falls, which is a *molybdate of molybdic oxide*, $MO_2.2MO_3$. This compound is likewise readily formed in a variety of other circumstances.

The salts of molybdic acid are colourless, when their base is not coloured. When they are treated with other acids, molybdic acid is precipitated, but dissolves in an excess of the acid. It forms both neutral and acid salts with the alkalies. These alkaline molybdates are the only ones that are easily soluble in water; of the rest, some dissolve sparingly, and others are completely insoluble. Solutions of the alkaline molybdates are coloured yellow by *hydrosulphuric acid* from formation of a sulphomolybdate of the alkali-metal (MS,MoS_3), and then yield with acids a brown precipitate of tersulphide of molybdenum. This is an extremely delicate test for molybdic acid. They form white precipitates with salts of the *earths*, and precipitates of various colours with salts of the heavy metals; *e. g.* white with *lead* and *silver* salts; yellow with *ferric* salts; and yellowish-white with *mercurous* salts.—*Protochloride of tin* produces immediately a greenish blue precipitate, soluble in hydrochloric acid forming a green solution; which turns blue on the addition of a very small quantity of the tin-solution.—When *tribasic phosphoric acid*, or a liquid containing it, is added to the

solution of molybdate of ammonia, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic acid combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The bibasic and monobasic phosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction. According to Seligsohn *, the yellow precipitate is a *phosphomolybdate of ammonia* $2(3NH_4O \,.\, PO_5) + 15(HO \,.\, 4MoO_3)$. By digesting it in a dilute solution of acetate of potash or soda, crystalline double salts are formed, containing $2(3NH_4O.PO_5) + 15\left(\left.\begin{matrix}KO \\ \text{or } NaO\end{matrix}\right\}.4MoO_3\right)$. With acetate of baryta, a double salt is formed, containing $3NH_4O.PO_5 + 30(BaO.MoO_3)$; and similarly with acetate of lead.

Molybdic acid and other compounds of molybdenum form a colourless bead with *borax* and *phosphorus-salt* in the outer blowpipe flame. In the inner flame, they form a brown bead with borax and a green bead with phosphorus-salt.

Molybdates of potash.—The *monomolybdate,* $KO.MoO_3$, is obtained by agitating the termolybdate with an alcoholic solution of potash: it then separates as an oily mass, which, when dried over lime and sulphuric acid, crystallises in four-sided prisms containing $2(KO.MoO_3) + HO$. It is also obtained by mixing a solution of molybdate of ammonia with excess of carbonate of potash, and evaporating to a syrup. Bimolybdate of potash does not appear to exist. When a solution of molybdic acid in carbonate of potash is mixed with strong nitric or hydrochloric acid till a slight permanent precipitate is produced, the liquid after a while yields crystals of a salt containing $4KO.9MoO_3 + 6HO$: and this salt is decom-

* J. pr. Chem. lxvii. 474.

posed by water into monomolybdate, which dissolves readily, and termolybdate which is sparingly soluble:

$$2(4KO.9MoO_3) = 3(KO.MoO_3) + 5(KO.3MoO_3).$$

The *termolybdate* dissolves easily in boiling water, and separates as a bulky white precipitate when the solution is quickly cooled; but by slow cooling it is obtained in needles, having a beautiful silky lustre and containing $KO.3MoO_3 + 3\ HO$. Nitric acid added in excess to a solution of molybdic acid in carbonate of potash throws down a white precipitate consisting sometimes of *quadromolybdate* and sometimes of *pentamolybdate* of potash, both anhydrous (Svanberg and Struve).*

Monomolybdate of soda, $NaO.MoO_3 + 2HO$, is obtained by fusing molybdic acid with an equivalent quantity of carbonate of soda. It is easily soluble in water, and crystallises in small rhombohedrons, which melt easily and give off their water. The *bimolybdate*, $NaO.2MoO_3 + HO$, is obtained in a similar manner. It crystallises in needles, and dissolves sparingly in cold, readily in boiling water. The *termolybdate* is obtained by adding nitric acid to a solution of molybdic acid in carbonate of soda, as a bulky white precipitate, more soluble than the corresponding potash-salt. The solution yields crystals containing $NaO.3MoO_3 + 7HO$. Nitric acid added in excess to a solution of molybdate of soda throws down nothing but molybdic acid (Svanberg and Struve).†

Monomolybdate of ammonia, $NH_4O.MoO_3$, obtained by treating molybdic acid in excess with strong solution of ammonia in a closed vessel, then precipitating with alcohol, and drying over quick lime, forms microscopic four-sided prisms, which are anhydrous. The *bimolybdate*, $NH_4O.2MoO_3$, is deposited as a white crystalline powder when a solution of molybdic acid in excess of ammonia is quickly evaporated. A solution of molybdic acid in ammonia, evaporated by heat to

* Ann. Ch. Pharm. lxviii. 494. † Ann. Ch. Pharm. lxviii. 404.

the crystallising point, or left to evaporate in the air, deposits large transparent six-sided prisms containing $NH_4O.2MoO_3 + NH_4O.3MoO_3 + 3HO$ (Svanberg and Struve).

Monomolybdate of baryta, $BaO.MoO_3$, is precipitated as a sparingly soluble crystalline powder on adding chloride of barium to a solution of molybdic acid in excess of ammonia. Baryta-salts, containing $BaO.3MoO_3 + 3HO$ and $BaO.2MoO_3 + BaO_2 3MoO_3 + 6HO$, are obtained by precipitating the corresponding potash and ammonia-salts with chloride of barium. By decomposing monomolybdate of baryta with dilute nitric acid, an acid salt is formed containing $BaO.9MoO_3 + 4HO$; it crystallises in small six-sided prisms, fusible and insoluble in water (Svanberg and Struve).

Monomolybdate of magnesia, $MgO.MoO_3 + 5HO$, is obtained in distinct crystals by boiling molybdic acid and *magnesia alba* with water, and evaporating the filtrate; it gives off 3 eq. water at 212° (Struve).*

Molybdate of manganous oxide, $MnO.MoO_3 + HO$, is obtained as a heavy white powder, by treating carbonate of manganese with termolybdate of potash or soda.

Protosulphate of iron added to a solution of molybdate of potash, reduces the molybdic acid to a lower state of oxidation; but if chlorine gas be passed through the solution at the same time, a bulky precipitate is formed, which, when dried in the air, forms a light yellow powder, consisting of *pentamolybdate of ferric oxide*, $Fe_2O_3.5MoO_3 + 16HO$.

By boiling the solution of termolybdate of potash or soda, or acid molybdate of ammonia, with hydrate of *alumina, manganic oxide, ferric oxide*, or *chromic oxide*, and evaporating to the crystallising point, double salts are obtained. The composition of the double salts containing alumina, ferric oxide, or chromic oxide with potash or oxide of ammonium, may be represented by that of the alumina and potash-salt, viz.,

* Ann. Ch. Pharm. xcvi. 266.

$Al_2O_3.6MoO_3 + 3(KO.2MoO_3) + 20HO$. The *potassio-manganic* salt contains $Mn_2O_3.6MoO_3 + 5(KO.2MoO_3) + 12HO$. The *ammonio-manganic* salt is similarly constituted. The *sodio-chromic* salt contains $Cr_2O_3.6MoO_3 + 3(NaO.2MoO_3) + 21HO$ (Struve).

Acid molybdate of ammonia, added to a boiling solution of sulphate of copper, throws down a heavy green amorphous powder, consisting of *basic molybdate of copper*, $4CuO.3MoO_3 + 5HO$. By adding molybdate of ammonia in excess to a cold solution of sulphate of copper, a double salt is formed, consisting of $CuO.2MoO_3 + NH_4O.3MoO_3 + 9HO$. It is a white-blue crystalline powder, which gives off 4 eq. of water at 212° and 4 eq. more at 266° (Struve).

Molybdate of lead, $PbO.MoO_3$, is formed by precipitating nitrate of lead with termolybdate of potash. It is a heavy white powder which melts only at a high temperature. It occurs finely crystallised as a mineral. Chromate of lead is dimorphous, and corresponds in the least usual of its forms with molybdate of lead: hence molybdenum is connected with the magnesian metals, and tungsten also with the same class, from the isomorphism of the tungstates and molybdates.

Sulphides of molybdenum.—The *bisulphide* is the ore from which the compounds of this metal are derived. It occurs in many parts of Sweden, and might be procured in quantity if any useful application of the metal were discovered. It is a lead-grey mineral, having the metallic lustre, composed of flexible laminæ, soft to the touch, and making a streak upon paper like plumbago. Nitric acid oxidates it easily, without dissolving it. Its density is from 4·138 to 4·569. A *tersulphide of molybdenum* is obtained in the same way as the corresponding compound of tungsten, and affords crystallisable sulphur-salts which are red. The sulphomolybdate of potassium combines likewise with nitrate of potash. When a solution of the former salt is boiled with tersulphide of molybdenum in excess, the latter is converted into bisulphide of

molybdenum, and a *quadrisulphide of molybdenum* dissolves in combination with the sulphide of potassium. The quadrisulphide may be precipitated by hydrochloric acid, and when dried is a cinnamon-brown powder.

Chlorides of molybdenum.—A *protochloride* is formed when molybdous oxide is dissolved in hydrochloric acid; the *bichloride* when molybdenum is heated dry in chlorine gas, as a dark-red gas which condenses in crystals, like those of iodine. It forms a crystallisable double salt with sal-ammoniac. *Chloromolybdic acid*, or a compound of terchloride of molybdenum and molybdic acid, MoO_2Cl, or $MoCl_3 + 2MoO_3$, is formed with (molybdic acid), when molybdic oxide is exposed to chlorine gas at a red heat. It sublimes below a red heat, and condenses in crystalline scales, which are white with a shade of yellow.

ESTIMATION OF MOLYBDENUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The determination of molybdic acid is more difficult than that of tungstic acid, on account of its partial volatility. The best mode of estimating it is to convert it into molybdic oxide by ignition in an atmosphere of hydrogen; the oxide which is perfectly fixed may then be weighed; it contains 74·95 per cent. of the metal. When molybdic acid exists in solution in ammonia or in other acids, the solution must be carefully evaporated to dryness, and the residue treated as above.

Molybdic acid is separated from most metallic oxides by its solubility in sulphide of ammonium. The filtered solution is then treated with an excess of very dilute nitric acid, to precipitate the tersulphide of molybdenum; the precipitate collected on a weighed filter, and its quantity determined; after which, a weighed quantity of it is ignited in an atmosphere of

hydrogen, to convert it into the bisulphide, MoS_2, from the weight of which the amount of molybdenum is calculated.

Molybdic acid is separated from the *earths* by fusing with carbonate of soda, and digesting the fused mass in water, which dissolves molybdate of soda, and leaves the earth in the form of carbonate.

From the *fixed alkalies*, molybdic acid may be separated by precipitation with mercurous nitrate, and its quantity estimated from the weight of the precipitate.

SECTION VII.

TELLURIUM.

Eq. 64·14 *or* 801·8 ; Te.

Tellurium is a metal of rare occurrence, and appeared at one time to be almost confined to certain gold mines in Transylvania; but it has been found lately, in considerable abundance, at Schemnitz, in Hungary, combined with bismuth; and in the silver mine of Sadovinski in the Altai, united with silver and with lead. It was first described as a new metal by Klaproth, who gave it the name of tellurium, from *tellus*, the earth.

Tellurium is chiefly obtained from telluride of bismuth. The ore, after being freed from the matrix by pounding and washing, is mixed with an equal weight of carbonate of potash or soda, the mixture made up into a paste with olive oil, and heated in a well closed crucible, carefully at first to prevent frothing, and afterwards to a full white heat. The fused mass is then digested in water; which leaves the bismuth and the excess of charcoal undissolved, and dissolves the tellurium in the form of telluride of potassium or sodium, which imparts a port-wine colour to the liquid. The solution deposits metallic tellurium when exposed to the air, or more

quickly when air is blown through it; and the precipitated metal is purified by washing with acidulated water, and subsequent distillation in an atmosphere of hydrogen (Berzelius). The metal is also obtained from the ore called *foliated tellurium*, which contains 13 per cent. of tellurium, and 63 per cent. of lead, together with copper, gold, antimony, and sulphur. The finely pounded mineral is freed from the sulphide of lead and antimony by repeated boiling with strong hydrochloric acid and washing with water; the residual telluride of gold treated with strong nitric acid; the tellurium-solution poured off from the gold and evaporated to dryness; the residue dissolved in hydrochloric acid; and the tellurium precipitated from the solution by sulphurous acid (Berthier).*

In a state of purity, tellurium is silver-white and very brilliant. It is very crystallisable, assuming a rhombohedral form, in which it is isomorphous with arsenic and antimony. It is brittle for a metal, and an indifferent conductor of heat and electricity. Its density is from 6·2324 to 6·2578, according to Berzelius. Tellurium is about as fusible as antimony, and may be distilled at a high temperature. It burns in air, at a high temperature, with a lively blue flame, green at the borders, and diffuses a dense white smoke, which generally has the odour of decaying horse-radish, from the presence of a little selenium. Tellurium belongs to the sulphur-class of elements. Like selenium and sulphur, it dissolves to a small extent in concentrated sulphuric acid, and communicates to it a fine purple-red colour. In this solution, the metal is not oxidated, for it is precipitated again, in the metallic state, by water. This metal has also considerable analogy with antimony, and may probably connect together the sulphur and

* For further details respecting the extraction of tellurium, vide Berzelius, Traité de Chimie, i. 344; and the translation of Gmelin's Handbook, iv. 393. Wöhler states, in a note to his paper on telluride of ethyl (Ann. Ch. Pharm. lxxxiv. 70), that tellurium may be obtained in considerable quantities from the residues of the Transylvanian gold-extraction, which have hitherto been thrown away as worthless.

phosphorus families. Tellurium combines in two proportions with oxygen, forming tellurous acid, TeO_2, and telluric acid, TeO_3.

Tellurous acid, TeO_2; 80·14 *or* 1001·8.—This acid differs remarkably in properties according as it is anhydrous or hydrated.* Hydrated tellurous acid is obtained by precipitating bichloride of tellurium with cold water; or by fusing anhydrous tellurous acid with an equal weight of carbonate of potash, as long as carbonic acid is disengaged, dissolving the tellurite of potash in water, and adding nitric acid to it till the liquor distinctly reddens litmus paper. A white and bulky precipitate is produced, which is washed with ice-cold water, and afterwards dried without artificial heat. Tellurium likewise dissolves with violence in pure nitric acid of density 1·25, and if after the first five minutes, the clear liquid be poured into water, tellurous acid is precipitated in white flocks. But if not immediately precipitated, the nitric acid solution undergoes a change.

The hydrated acid obtained by these processes forms a light, white, earthy mass, of a bitter and metallic taste. It instantly reddens litmus paper, and while still moist, dissolves to a sensible extent in water. It is very soluble in acids, and the solutions are not subject to change, except that which is formed by nitric acid. Ammonia and the alkaline carbonates also dissolve hydrated tellurous acid with facility, the latter becoming bicarbonates.

Anhydrous tellurous acid.—When the solution of tellurous acid in water is heated to 140°, it deposits the anhydrous acid in grains, and loses its acid reaction. The same change occurs when an attempt is made to dry the hydrated tellurous acid by heat: it parts with combined water, and becomes granular. The solution of tellurous acid in nitric acid changes spon-

* Berzelius regarded the hydrated and anhydrous acids as containing different modifications of the same compound, and distinguished them as α-tellurous and β-tellurous acid.

taneously in a few hours, and in a quarter of an hour when heat is applied to it, and allows the anhydrous acid to precipitate. When the deposition of the acid is slow, it forms a crystalline mass of fine grains, among which octohedral crystals may be perceived by the microscope. The acid is then anhydrous. In this state it does not redden litmus, or not till after a time. It is but very slightly soluble in water, and the solution has no acid reaction. At a low red heat, it fuses into a clear transparent liquid of a deep yellow colour, which on cooling becomes a white and highly crystalline mass, easily detached from a crucible. Tellurous acid is volatile, although less so than the metal itself.

The solutions of hydrated tellurous acid in the stronger acids yield a black precipitate of metallic tellurium, when treated with powerful deoxidising agents, such as zinc, phosphorus, protochloride of tin, sulphurous acid, and the alkaline bisulphates. Hydrosulphuric acid and sulphide of ammonium throw down black-brown sulphide of tellurium, easily soluble in excess of sulphide of ammonium.

The *tellurites*, or compounds of tellurous acid with salifiable bases, contain 1 atom of base united with 1, 2, or 4 atoms of acid. They are fusible, and generally solidify in the crystalline form on cooling; the quadrotellurites, however, form a glass. Tellurites are colourless unless they contain a coloured base; those which are soluble have a metallic taste. Most of them, when heated to redness with charcoal, yield metallic tellurium, sometimes with slight detonation; and the reduced metal volatilises readily, being at the same time reoxidised and forming a white deposit on the charcoal; it likewise imparts a green colour to the flame; the tellurites, when ignited with potassium, or with charcoal and carbonate of potash, yield telluride of potassium which dissolves in water, forming a port-wine coloured solution; with the zinc and silver-salts, however, and a few others, this reduction does not take place. The tellurites of ammonia, potash and soda are easily soluble

in water; those of baryta, strontia, and lime are sparingly soluble; the rest, insoluble. An aqueous solution of a tellurite is decomposed by the carbonic acid of the air. Nearly all tellurites dissolve in strong hydrochloric acid without evolving chlorine when heated; the solution exhibits the above-mentioned characters of a solution of tellurous acid in the stronger acids, except in so far as it may be interfered with by the presence of another base. The solution when diluted in water yields a white precipitate of tellurous acid, provided the excess of hydrochloric acid present is not too great.

Monotellurite of potash, $KO.TeO_2$, is obtained by heating 1 eq. tellurous acid with eq. of carbonate of potash. The fused mass on cooling forms crystals of large size. The salt dissolves slowly in cold, more quickly in warm water. *Bitellurite of potash*, $KO.Te_2O_4$, is obtained by fusing two atoms of tellurous acid with one atom of carbonate of potash. It appears to be capable of existing in a hot solution, and of crystallising in certain circumstances; but it is decomposed by cold water, which resolves it into the neutral salt, which dissolves, and a *quadritellurite of potash*, $KO.Te_4O_8 + 4HO$. The latter salt cannot be redissolved in water, without decomposition. In losing its water when heated, it swells up like borax.

Telluric acid, TeO_3; 88·14 *or* 1101·8.—This acid is obtained in combination with potash, by fusing tellurous acid with nitre. It may then be transferred to baryta, and the insoluble tellurate of baryta decomposed by sulphuric acid. The solution of telluric acid gives bulky, hexagonal, prismatic crystals. Its taste is not acid, but metallic, resembling that of nitrate of silver. Indeed, it appears to be but a feeble acid, reddening litmus but slightly, when the solution is diluted. The crystallised acid contains 3HO, of which it loses 2HO by efflorescence, a little above 212°. It then appears insoluble in cold water, but may be completely redissolved by long digestion, particularly with ebullition, and is not permanently altered.

Anhydrous telluric acid.—The crystals of hydrated telluric acid give off all their water at a heat below redness, and are converted into a mass of a fine orange-yellow colour, without changing their form. This yellow matter, which is distinguished, as *alpha-telluric acid* by Berzelius, is remarkable for its indifference to chemical reagents, being completely insoluble in cold or boiling water, in hot hydrochloric and nitric acids, and in potash-ley. At a high temperature, it is decomposed, evolving oxygen, and leaving tellurous acid white and pulverulent.

Telluric acid has but slight affinity for bases. The hydrated acid withdraws from alkaline carbonates, only so much alkali as to form a biacid salt. Telluric acid forms bibasic, sesquibasic, monobasic, biacid, and quadracid salts. The tellurates are colourless, unless they contain a coloured base. At a red heat, they give off oxygen and are converted into tellurites. Before the blowpipe, they behave like the tellurites; also with reducing agents, such as protochloride of tin, and sulphurous acid, excepting that the reduction does not take place so quickly, and in some cases requires the application of heat. Hydrosulphuric acid, added to the solution of a tellurate, produces no change at first; but if the liquid be placed in a stoppered bottle and left for a while in a warm place, a brown precipitate of sulphide of tellurium is formed. Tellurates dissolve in cold strong hydrochloric acid without decomposition. The solutions are not yellow, like those of the tellurites in hydrochloric acid, and may be diluted with water without becoming milky, even though the excess of hydrochloric acid be but small. But on boiling the solution, chlorine is evolved, and the liquid, if subsequently mixed with water, gives a precipitate of tellurous acid, provided the excess of hydrochloric acid is not too great.

Neutral *tellurate of potash* is $KO.TeO_3 + 5HO$; the *bitellurate of potash*, $KO.Te_2O_6 + 4HO$; the *quadritellurate of potash*, $KO.Te_4O_{12} + 4HO$. All these salts may be obtained

directly, in the humid way, by dissolving the proper proportions of hydrated acid and carbonate of potash together, in hot water. A portion of the combined water in the last two salts is unquestionably basic, but how much of it is so has not been determined. They cannot be made anhydrous by heat without being essentially altered in properties.

The neutral tellurate of potash undergoes no change in constitution under the influence of heat, resembling in that respect those tribasic phosphates of which the whole three atoms of base are fixed. The bitellurate of potash loses its water and becomes yellow at a temperature below redness, and is changed into a quadritellurate, which is insoluble both in water and in dilute acids. Water dissolves out neutral tellurate from the yellow mass. The insoluble salt is named, by Berzelius, the *alpha-quadritellurate* of potash. The elements of this compound are united by a powerful affinity. It is formed when hydrated telluric acid is intimately mixed with a potash-salt, such as nitre or chloride of potassium, and the mixture calcined at a temperature which should be much below a red heat; also when tellurous acid is ignited with chlorate of potash, and in other circumstances. Hydrate of potash dissolves the alpha-quadritellurate by fusion, and nitric acid by a long continued ebullition; but in both cases, the acid set free in the solution exhibits the properties of ordinary telluric acid.

Telluretted hydrogen, Hydrotelluric acid, TeH, is a gaseous compound of tellurium and hydrogen, analogous in constitution and properties to sulphuretted hydrogen. It is obtained by fusing tellurium with zinc or with tin, and acting on the mixture with hydrochloric acid.

Definite *sulphides of tellurium* have been obtained, corresponding with tellurous and telluric acids. They are sulphur-acids.

Two *chlorides of tellurium* have been formed, a protochloride, TeCl, to which there is no corresponding oxide, and a bichlo-

ride, $TeCl_2$. No higher chloride, corresponding with telluric acid, has been obtained.

Tellurium forms alloys with several metals, *e.g.*, with potassium, sodium, aluminum, bismuth, zinc, tin, lead, iron, copper, mercury, silver, and gold. Some of these alloys, as those of bismuth, silver, and gold, are found native.

Telluride of potassium is prepared by mixing 1 part of tellurium powder with 10 parts of burnt tartar; introducing the mixture into a porcelain retort fitted with a glass tube bent downwards at right angles; heating the retort to redness for three or four hours, as long, indeed, as carbonic oxide continues to escape; and then introducing the end of the bent tube into a flask kept full of carbonic acid gas, to prevent access of air; this latter precaution is necessary on account of the highly pyrophoric character of the product (Wöhler). The compound may also be obtained by heating tellurium with potassium, in a retort filled with hydrogen; combination then takes place attended with vivid combustion. Telluride of potassium dissolves in water, forming a port-wine coloured solution, which on exposure to the air becomes decolorised, and deposits tellurium in shining scales; with acids it evolves telluretted hydrogen gas. *Telluride of sodium* is prepared by similar methods, and possesses similar properties.

ESTIMATION OF TELLURIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

When tellurium exists in solution in the form of tellurous acid it is reduced to the metallic state by sulphurous acid or an alkaline bisulphite. The reduced tellurium is then collected on a weighed filter, and carefully dried at gentle heat. If the solution is alkaline, it must be previously acidulated with hydrochloric acid; if it contains nitric acid, which might redissolve a portion of the precipitated tellurium, it must be boiled

with hydrochloric acid till all the nitric acid is decomposed, then diluted with water, and treated with sulphurous acid as above. If the tellurium is in the state of telluric acid, that compound must first be reduced to tellurous acid by boiling with hydrochloric acid, and the tellurium then reduced by sulphurous acid.

Tellurium may be separated from the *alkalies* and *earths*, and from *manganese, iron, cobalt, nickel, zinc,* and *chromium,* by means of hydrosulphuric acid. If the precipitated sulphide of tellurium is quite pure and definite, it may be collected on a weighed filter, dried and weighed, and the amount of tellurium calculated from it. But if it contains excess of sulphur, which is often the case, it must be boiled with aqua-regia till it is completely decomposed; the solution filtered from the separated sulphur; freed from nitric acid in the manner above described; and the tellurium precipitated by sulphurous acid.

The separation of tellurium from *cadmium, copper,* and *lead,* may be effected by means of sulphide of ammonium, in which the sulphide of tellurium is easily soluble. The filtered solution is then treated with excess of hydrochloric acid to precipitate the sulphide of tellurium, which is then decomposed by aqua-regia as just described. Tellurium may be separated from *tin* in solution by means of sulphurous acid.

The quantity of metallic tellurium in an alloy may be estimated by heating the alloy in a current of chlorine gas; passing the volatile chloride of tellurium into water acidulated with hydrochloric acid, which dissolves it; and reducing the tellurium by sulphurous acid.

6

ORDER VI.

METALS ISOMORPHOUS WITH PHOSPHORUS.

SECTION I.

ARSENIC.

Eq. 75 *or* 937·5.

This metal is found native, but more generally in combination with other metals, particularly cobalt and nickel, and is largely condensed, during the roasting of their ores, in the state of arsenious acid. The metal may be easily obtained, in a state of purity, by subliming a portion of native arsenic in a glass tube or retort, by the heat of a lamp, or by reducing a mixture of one part of arsenious acid and three parts of black flux, in the same apparatus. The metal in condensing forms a crust, of a steel-grey colour and bright metallic lustre. It has been observed to crystallise by sublimation in rhombohedral crystals, and is isomorphous with tellurium and antimony. It is a brittle metal, and very easily pulverised. The density of arsenic is from 5 to 5·96. It rises in vapour at 356° (180° Cent.) without first undergoing fusion. Arsenic vapour is colourless; its density is 10·370; and, like phosphorus and oxygen, its combining measure is one volume. It has as strong an effect upon the organ of smell as selenium; its odour resembles that of garlic. Arsenic combines in three proportions with oxygen, forming by spontaneous oxidation in air a grey sub-oxide, the composition of which is undetermined; it also forms arsenious and arsenic acids, AsO_3 and AsO_5.

Arsenious acid, 99 *or* 1237·5.—This compound is formed when metallic arsenic is volatilised in contact with the air. It is obtained in large quantity, as an accessary product, in the roasting of arsenical ores of tin, cobalt, and nickel, and as principal product in the roasting of arsenical pyrites. These operations are performed in reverberatory furnaces, communicating with chambers in which the arsenious acid condenses. The product is purified by a second sublimation in vessels of cast-iron, or, on a small scale, in glass or earthen retorts.

Arsenious acid heated in a tube closed at both ends melts into a colourless liquid; but under the ordinary atmospheric pressure, it volatilises at about 380° (at 444° according to Mitchell), without previous fusion, producing a colourless vapour, which has a density of 13·850, and is therefore composed of 1 volume of arsenic vapour and 3 volumes of oxygen, condensed into 1 volume. The vapour is inodorous when pure, but if the acid be volatilised in contact with any easily oxidisable substance, as when it is thrown on red-hot coals or iron, the garlic odour of metallic arsenic becomes perceptible.

In the solid state, arsenious acid exhibits three modifications, one amorphous, and two crystalline. (1.) When the sides of the vessel in which the acid is distilled become strongly heated, the vapour condenses, at a temperature near the melting point of the acid, into a transparent vitreous mass, having a conchoïdal fracture. (2.) When arsenious acid is sublimed in a glass tube, or under any circumstances which allow the vapour to condense suddenly, and solidify at once, without passing through the semi-fused state, it assumes the form of regular octohedrons, which, if the sublimation be slowly conducted, are distinct, and have an adamantine lustre. Similar octohedral crystals are obtained when arsenious acid separates from its solution in water or in ammonia. (3.) In the roasting of arsenical cobalt ores, arsenious acid is sometimes obtained in the form of thin transparent flexible plates,

derived from a right rhombic prism (Wöhler). Crystals of similar form are obtained by saturating a boiling solution of caustic potash with arsenious acid, and then leaving it to cool or mixing it with water (Pasteur). Vitreous arsenious acid, even when completely protected from air and moisture, gradually loses its transparency, and becomes an opaque white mass, passing in fact into the octohedral variety.

The specific gravity of transparent vitreous arsenious acid is 3·7385, that of the octohedral variety 3·699 (Guibourt). The vitreous acid dissolves in water more quickly and more abundantly than the opaque crystalline acid; the same quantity of water which at 54° or 55° will take up 36 or 38 parts of the former, will not take up more than 12 or 14 of the latter (Bussy). According to Guibourt, on the contrary, 100 parts of boiling water dissolve 9·68 parts of the vitreous, and 11·47 of the opaque acid; and when the solutions are left to cool to 60°, the first retains 1·78 parts, and the latter 2·9 parts of the acid. The discrepancy of these statements and of various others respecting the solubility of arsenious acid, may perhaps be reconciled by the great facility with which the amorphous variety passes into the crystalline, and *vice versa.* It appears indeed that heat tends to transform the opaque into the vitreous acid, and cold to produce the contrary change, and this tendency is manifested even in presence of water. Thus the opaque acid is converted into the vitreous by long boiling with water, the contrary change taking place gradually in the solution when cold.

The aqueous solution of arsenious acid is transparent and colourless, and reddens litmus slightly. *Hydrosulphuric acid* colours it yellow, and on the addition of hydrochloric acid throws down a yellow precipitate of AsS_3. On the addition of a small quantity of ammonia, it gives a yellow precipitate with nitrate of *silver,* and a peculiar light green (Scheele's green) with sulphate of *copper;* these precipitates are easily soluble in excess of ammonia. Mixed with hydrochloric acid

it produces a grey metallic deposit on *copper*. With *zinc* and sulphuric or hydrochloric acid, it evolves arseniuretted hydrogen gas (p. 211.).

Arsenious acid dissolves in many acids, in hydrochloric acid for example, with much greater facility than in water, but without forming any definite compounds. It is dissolved, however, by bitartrate of potash, with formation of a crystallisable salt analogous to the potash-tartrate of antimony. The vitreous acid dissolved in boiling dilute hydrochloric acid crystallises on cooling in regular octohedrons, the deposition of each crystal being accompanied by a flash of light. Agitation increases the number of crystals produced, and the intensity of the light. The opaque acid dissolved in hydrochloric acid does not emit any light on crystallising; the same is the case with the crystals obtained by cooling a solution of the vitreous acid in hydrochloric acid, when these crystals are redissolved in hydrochloric acid. Hence it appears that the vitreous acid dissolves *as such* in hydrochloric acid, and that the emission of light at the moment of crystallisation is due to the change from the amorphous to the crystalline state.

Arsenious acid is dissolved by *potash, soda,* and *ammonia,* also by *alkaline carbonates,* but from these latter solutions it is sometimes deposited in the free state, so that it is doubtful whether arsenious acid displaces carbonic acid in the humid way. The arsenites of the earths and metallic oxides are insoluble in water, but soluble in acids.

With potash, arsenious acid forms the salts $2KO . AsO_3$, $KO . AsO_3$, and $KO . HO . 2AsO_3$; similar salts with soda. With baryta, it forms $2BaO . AsO_3$ and $BaO . AsO_3$; and with lime, $2CaO . AsO_3$. With nickel, cobalt, and silver, it forms bibasic and sesquibasic salts.

The neutral solutions of the alkaline arsenites give a yellow precipitate with nitrate of *silver*, and Scheele's green with *copper* salts. Acidulated with hydrochloric acid, they give

with *hydrosulphuric acid,* &c., the same reactions as aqueous arsenious acid.

Nitric acid and *aqua regia* transform arsenious into arsenic acid. *Hydrogen, charcoal,* and other reducing agents easily reduce it to the metallic state.

Arsenious acid has a rough taste, slightly metallic, and afterwards sweetish. It is one of the most violent among acrid poisons.

The principal industrial use of arsenious acid is in calico-printing; it is also used in glass-making, serving to transform the protoxide of iron into sesquioxide, which produces glasses less highly coloured than the protoxide.

Arsenic acid, AsO_5, 115 *or* 1437·5.—This acid is obtained by heating powdered arsenious acid in a basin with an equal quantity of water, and adding nitric acid in small quantities to the mixture at the boiling point, so long as ruddy fumes escape. An addition of hydrochloric acid to the water is generally made, to increase the solubility of the arsenious acid, but it is not absolutely necessary. The solution of arsenic acid is then evaporated to dryness, to expel the remaining nitric and hydrochloric acids; but the dry mass must not be heated above the melting point of lead, otherwise oxygen gas is emitted and arsenious acid reproduced. Arsenic acid thus obtained is milk-white, and contains no water. Exposed to air, it slowly deliquesces, and runs into a liquid. But notwithstanding this, when strongly dried, it does not dissolve completely in water at once, and a portion of it appears to be insoluble; but the whole is dissolved by continued digestion. Arsenic acid, in absorbing moisture from the air, sometimes forms hydrated crystals, which are highly deliquescent; but this acid is easily made anhydrous, and does not retain basic water with force, like phosphoric acid. Its solution has a sour taste, and reddens vegetable blues. Arsenic acid, indeed, is a strong acid, and with the aid of heat expels all the volatile

acids from their combinations. Arsenic acid undergoes fusion at a red heat, and at a higher temperature is completely dissipated in the form of arsenious acid and oxygen.

When an equivalent of arsenic acid is ignited with an excess of carbonate of soda, three equivalents of carbonic acid are expelled, and a *tribasic arseniate of soda* formed, which when dissolved in water, crystallises with 24 equivalents of water, forming the salt $3NaO . AsO_5 + 24HO$, isomorphous with the subphosphate of soda. The same salt is obtained by treating arsenic acid in solution with an excess of caustic soda. When carbonate of soda is added to a hot solution of arsenic acid, so long as there is effervescence, a salt is obtained by evaporation corresponding with the common phosphate of soda, containing 2 eq. of soda and 1 eq. of water as bases. This salt affects the same two multiples, in its water of crystallisation, as phosphate of soda, namely, $24HO$ and $14HO$, but most frequently assumes the smaller proportion, forming the salt $2NaO . HO . AsO_5 + 14HO$. This arseniate is more soluble than the phosphate, and slightly deliquescent in damp air. When to the last salt a quantity of arsenic acid is added equal to that which it already contains, and the solution is highly concentrated, the salt named *biarseniate of soda* crystallises at a low temperature. This salt contains 1 eq. of soda and 2 eq. of water as bases, with 2 eq. of water of crystallisation, and corresponds with the biphosphate of soda. Its formula is $NaO.2HO.AsO_5 + 2HO$. The *biarseniate of potash*, which is analogous in composition, is a highly crystallisable salt. It is sometimes prepared by deflagrating arsenious acid with an equal weight of nitrate of potash. These arseniates of the alkalies, which contain water as base, all lose that element at a red heat; but, unlike the phosphates, they recover it when redissolved in water. Arsenic acid, therefore, forms only one, and that a tribasic class of salts. The arseniates of the earths and other metallic oxides are insoluble in water, but soluble in acids. *Arseniate of silver* ($3AgO . AsO_5$) falls as a preci-

pitate of a chocolate-brown colour, when nitrate of silver is added to the solution of an arseniate, and affords an indication of the presence of arsenic acid. On treating a solution of arsenic acid with *ammonia* in excess, *chloride of ammonium,* and *sulphate of magnesia,* a white crystalline precipitate is formed, consisting of arseniate of magnesia and ammonia, $2MgO . NH_4O . AsO_5 + 12$ Aq., similar in appearance and analogous in constitution to the ammonio-magnesian phosphate. *Hydrosulphuric acid* produces a yellow precipitate of AsS_5 after a considerable time; but if the solution be previously mixed with sulphurous acid, which reduces the arsenic acid to arsenious acid, a precipitate of AsS_3 is immediately produced.

Sulphides of arsenic.—When the bisulphide, realgar, is digested in caustic potash, it gives off sulphur and leaves a brownish black powder, having some resemblance to bioxide of lead, which, according to Berzelius, is the sulphide As_6S. *Bisulphide of arsenic,* AsS_2, is obtained by fusing sulphur with an excess of arsenic or arsenious acid. It is transparent and of a fine ruby colour after cooling, and may be distilled without decomposition. It forms the crystalline mineral realgar. *Sulpharsenious acid,* or *orpiment,* AsS_3, also occurs native. It may be prepared by decomposing a solution of arsenious acid in hydrochloric acid, by hydrosulphuric acid or by an alkaline sulphide. This sulphide has a rich yellow colour, and is the basis of the pigment called *king's yellow.* It is insoluble in acids, but soluble to a small extent in water containing hydrosulphuric acid, and also in pure water, but is precipitated by ebullition with a little hydrochloric acid. When heated, it fuses readily and becomes crystalline on cooling. It is readily dissolved by ammonia and solutions of the fixed alkalies, and is indeed a powerful sulphur-acid. *Sulpharsenic acid,* AsS_5, falls as a yellow precipitate, having much the appearance of orpiment, when a solution of arsenic acid somewhat concentrated is decomposed by hydrosulphuric acid. It may be sublimed

without change, and after cooling forms a non-crystalline mass. It is also a powerful sulphur-acid, forming salts called *sulpharseniates*. *Persulphide of arsenic*, AsS_{18}, is obtained by precipitating neutral solution of sulpharseniate of potassium with alcohol, filtering the liquid, and evaporating off two-thirds of the alcohol; the concentrated solution, when left to cool, deposits the persulphide of arsenic in shining yellow crystalline laminæ.

Chlorides of arsenic.—A *terchloride*, $As\,Cl_3$, corresponding with arsenious acid, is formed when arsenic is introduced into chlorine gas, in which it takes fire and burns spontaneously. The same compound is obtained by distilling a mixture of 1 part of arsenic with 6 parts of corrosive sublimate; also by distilling arsenious acid with excess of hydrochloric acid, or of common salt and sulphuric acid. It is a colourless, oily, and very dense liquid, which is resolved by water into arsenious and hydrochloric acids. When a mixture of arsenic and calomel is distilled, a dark brown sublimate is formed, consisting partly of Hg_2ClAs, partly of Hg_4ClAs. No chloride corresponding with arsenic acid is known. *Bromide of arsenic*, $AsBr_3$, is formed by the direct combination of its elements. *Iodide of arsenic*, $As\,I_3$, is formed, according to Plisson, by digesting 3 parts of arsenic with 10 of iodine and 100 of water, as long as the odour of iodine is perceived. The liquid yields by evaporation red crystals of the iodide. *Fluoride of arsenic*, AsF_3, is obtained by distilling a mixture of fluor spar and arsenious acid with sulphuric acid. It is a fuming, colourless liquid; the density of its vapour is 2730 (Unverdorben).

Arsenic and hydrogen.—A solid arsenide of hydrogen was obtained by Davy, by using metallic arsenic as the negative pole (the chloroid) in decomposing water. Gay-Lussac and Thénard have also shown that the same compound precipitates when arsenide of potassium is dissolved in water. It is a chestnut-brown powder, which may be dried without change.

Its composition has not been determined with accuracy. *Arseniuretted hydrogen*, AsH_3, a gas analogous in constitution to ammonia, is obtained by dissolving arseniate of potassium or sodium in water, or an alloy of equal parts of zinc and arsenic in sulphuric acid diluted with three times its weight of water; or again, when zinc dissolves in hydrochloric or dilute sulphuric acid, with which arsenious acid is mixed:

$$6Zn + 3HO + AsO_3 + 6SO_3 = 6(ZnO \, . \, SO_3) + AsH_3.$$

It is a dangerous poison, when inhaled even in the most minute quantity, and should, therefore, be prepared with the greatest caution. The density of this gas is 2695 (Dumas). It is liquefied by a cold of —40°. When passed through a glass tube heated to redness by a spirit lamp, it is decomposed and deposits metallic arsenic. The flame of this gas, when burned in air, also deposits metallic arsenic upon a cold object exposed to it. No combination of arseniuretted hydrogen is known with either acids or bases. It precipitates many of the metallic solutions which are precipitated by hydrosulphuric acid, but not oxide of lead, its hydrogen alone being oxidated, and the arsenic being precipitated in combination with the metal. From the salts of silver, gold, platinum, and rhadium, it precipitates the metals, while arsenious acid remains in solution. This gas, when pure, is completely absorbed by a solution of sulphate of copper, and $AsCu_3$ precipitated.

TESTING FOR ARSENIC.

Poisoning from arsenious acid is much more frequent than from any other substance. Hence, a more than usual degree of importance is attached to the modes of detecting the presence of arsenic in minute quantity. Of the different preparations of the metal, arsenic acid, and after it arsenious acid,

are the most poisonous; the salts and sulphides are so in a much less degree. Arsenious acid in the solid form and unmixed with foreign matters, is easily recognised as a white heavy powder, which is tasteless or nearly so, is entirely volatilised by heat, and diffuses a garlic odour in the reducing flame of a lamp. When dissolved in water, arsenious acid may be detected by the fluid tests, already mentioned (pp. 205, 206.). The silver and copper tests are most conveniently applied in the following forms.

1. *Ammonio-nitrate of silver.*—This is an exceedingly delicate test of arsenious acid, whether free, or in combination with an alkali. It is prepared by adding diluted ammonia to a solution of nitrate of silver, till the oxide of silver, which is first thrown down, is redissolved. When the ammonia has been added in proper quantity and not in excess, the odour of that substance is scarcely perceptible, and the liquid contains in solution the crystallisable ammonio-nitrate of silver, $AgO.NO_5 . 2NH_3$. This test-liquid throws down from arsenious acid, the yellow arsenite of silver, which is redissolved both by acids and by ammonia. A solution of nitrate of silver gives the same indication as the prepared ammonio-nitrate in an alkaline but not in an acid solution of arsenious acid. Nitrate of silver produces, in phosphate of soda or any other soluble phosphate, a yellow precipitate of phosphate of silver of the same colour as the arsenite of silver, and which might, therefore, be mistaken for the latter; but the action of the ammonio-nitrate is not liable to that ambiguity, as it does not produce a yellow precipitate in an alkaline solution of phosphoric acid, the phosphate of silver being then retained in solution by the ammonia of the reagent, although arsenite of silver is precipitated in the same circumstances. Both phosphate and arseniate of silver are indeed considerably more soluble in ammonia than the arsenite of the same metal.

2. *Ammonio-sulphate of copper* gives a beautiful green precipitate, the arsenite of copper, in both alkaline and acid solu-

tions of arsenious acid; sulphate of copper gives the same precipitate in the former, but not in the latter.

But in solutions containing organic matter, the indications of these tests are sometimes delusive, and often doubtful. Recourse is then had to the proper means of obtaining arsenic in the metallic form, from the liquid suspected to contain arsenious acid. Indeed, even where the indications of the fluid tests are clear, the reduction test should never be omitted, the evidence which it affords being of a superior and completely demonstrative character. The reduction test of arsenic is practised in two different ways: (1.) by the reduction of the sulphide of arsenic by means of charcoal and carbonate of potash, and (2.) by the production, and subsequent decomposition of the gaseous compound of arsenic and hydrogen. The following operations are necessary in the practice of the first method :—

REDUCTION TEST OF ARSENIC.

I. Preparation of the fluid :

1. Heat the mass with about one-fourth of its weight of strong sulphuric acid in a retort, to which is adapted a receiver having its inner surface wetted, till the organic matter is carbonised.
2. Pulverise the residue, and treat it with nitric acid mixed with a little hydrochloric acid, in order to bring the arsenic to the state of arsenic acid, which is easily soluble.
3. Boil with water; filter; and mix the filtrate with the liquid in the receiver.*

* This is the mode of preparation most generally adopted, and it is applicable to all cases of searching for mineral poisons. Another method, which is especially applicable when the matter to be examined contains a large quantity of fat, is to heat the mass with strong hydrochloric acid, or aqua-regia, in

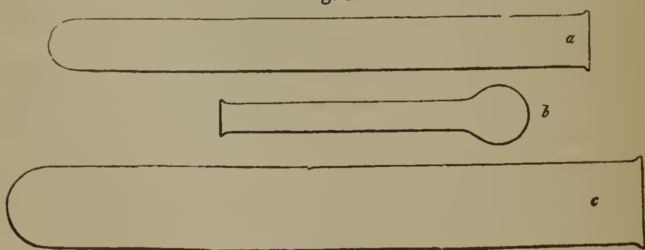
II. Precipitation of the sulphide of arsenic:

1. Transmit a stream of hydrosulphuric acid gas through the liquid for half an hour.*
2. Heat the liquid in an open vessel for a few minutes, to cause the precipitate to separate.
3. Wash the precipitate by affusion of water acidulated with hydrochloric acid, and subsidence.
4. Dry the precipitate at a temperature not exceeding 300°.

III. Reduction of the sulphide of arsenic:

1. Mix the dried precipitate intimately with twice its bulk of dry black flux (carbonate of potash and charcoal), or with a mixture of pounded charcoal and dry carbonate of soda, or with cyanide of potassium, and heat to redness in a glass tube, of the form and size of *a* or *b*, exhibited below.
2. Heat slowly a particle of the metallic crust in a glass tube *c*, and observe the formation of a white crystalline sublimate of arsenious acid.
3. Dissolve the sublimate in a small quantity of boiling water, and test with ammonio-nitrate of silver, &c., as above.

Fig. 8.

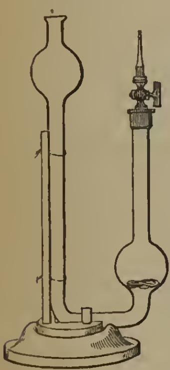


a large retort; the greater part of the arsenic is then converted into chloride, and may be collected in a receiver containing water.

* As the arsenic is in the state of arsenic acid, it is best to mix the liquid with sulphurous acid before passing the hydrosulphuric acid gas through it.

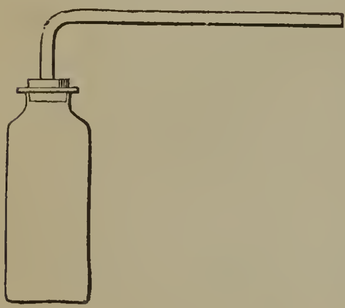
Marsh's test.—Hydrogen cannot be evolved in contact with any preparation of arsenic, soluble or insoluble, without combining with the metal, which is thus removed from the liquor, in the form of arseniuretted hydrogen gas. Mr. Marsh has founded, upon this fact, a simple and elegant mode of obtaining metallic arsenic from arsenical liquors. The stopcock being removed from the bulb-apparatus represented in the figure, a fragment of zinc is placed in the lower bulb, and diluted sulphuric acid poured upon it. The stopcock being replaced and closed, the lower bulb is soon filled with hydrogen gas, and the acid liquid forced into the upper bulb. It is necessary to test this hydrogen for arsenic, which will be found in it, if the zinc itself contains that metal. The gas for this purpose is kindled at the stopcock and allowed to burn with a small flame. If a stoneware plate be depressed upon the flame, a black spot of a steel-grey colour and bright metallic lustre, is formed, in a few seconds, upon the surface of the plate, supposing the gas to contain arsenic; or if a cold piece of glass be held over the flame, at a small height above it, a white sublimate of arsenious acid condenses upon the glass. But if the zinc employed contains no arsenic, neither of these effects is produced. The zinc being proved to be free from arsenic, a portion of the liquor to be tested is introduced into the lower bulb, in addition to the acid and zinc already there; and when the bulb is again filled with hydrogen gas, the latter is burned and examined precisely as before. If the liquor is loaded with organic matter, as generally happens with the liquids submitted to examination in actual cases of poisoning, the gas may be filled with froth, and the evolution of it very slow. But in the course of a night, the gas is

Fig. 9.



generally obtained in sufficient quantity, and in a proper state, to permit of examination. It is much better, however, first to remove the organic matter by one of the methods above given; the gas is then evolved freely and without frothing, and a plain bottle with a cork and glass jet will be sufficient for this reduction experiment. Then also, instead of burning the gas at the jet, it may be allowed to escape by a horizontal tube, such as that in figure 10., a portion of which is heated to redness by a spirit lamp. The arsenic condenses within the tube, beyond the flame and nearer the aperture, and forms a metallic crust, which may be converted by sublimation into arsenious acid; the sublimate may then be dissolved in a small quantity of boiling water, and the solution tested with ammonio-nitrate of silver, &c., as before.

Fig. 10.



When the liquid examined contains antimony, that metal combines with the nascent hydrogen, and comes off as antimoniuretted hydrogen, a gas which, when burned, or heated in a glass tube, gives the metal and a white sublimate, in the same circumstances as arsenic (L. Thompson). Antimony, however, may be recognised by a peculiarity of its reduction in the ignited tube. This metal is deposited in the tube, on both sides of the heated portion of it, and closer to the flame than arsenic, owing to the inferior volatility of antimony. The white sublimate also, if dissolved in water containing a drop of ammonia, will not give the proper indications with the fluid tests of arsenic, if the metal be antimony. Another distinction is, that the arsenical deposit is soluble in hypochlorite of soda, whereas the antimonial deposit is not.

Antidotes to arsenious acid.—When hydrated sesquioxide of iron is mixed with a solution of arsenious acid to the consistence of a thin paste, a reaction occurs by which the arsenious acid disappears in a few minutes, and the mass ceases to be poisonous. The arsenious acid takes oxygen from the sesquioxide of iron, and becomes arsenic acid, while the sesquioxide of iron is reduced to protoxide, a protarseniate of iron being the result, which is insoluble and inert:

$$2Fe_2O_3 + AsO_3 = 4FeO \, . \, AsO_5.$$

The constitution of this arseniate of iron is probably $2FeO.HO.AsO_5 + 2FeO$. Sesquioxide of iron, when used as an antidote to arsenious acid, should be in a gelatinous state, as it is obtained by precipitation, without drying. It may be prepared extemporaneously, by adding bicarbonate of soda in excess to any tincture or red solution of iron. Calcined magnesia may likewise be used as an antidote to arsenic. Care should be taken in preparing the latter not to employ too great a heat, which would render it very dense, and cause it to combine but slowly with the arsenious acid.

ESTIMATION OF ARSENIC, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

When arsenic is contained in a solution entirely in the form of arsenic acid, the best mode of estimating it is to precipitate it in the form of ammonio-magnesian arseniate, $2MgO \, . \, NH_4O \, . \, AsO_5 + 12HO$. The solution is mixed with excess of ammonia, and then with sulphate of magnesia, to which a quantity of chloride of ammonium has been added, sufficient to prevent the precipitation of the magnesia by ammonia. The liquid is then left to stand for about twelve

hours; the precipitate collected on a weighed filter; washed with water containing ammonia; and dried over sulphuric acid in vacuo at ordinary temperatures; it has then the composition expressed by the above formula. It may also be dried, and more expeditiously, by exposing it to a temperature of exactly 212° F., whereby it loses 11 eq. of water, and is reduced to $2MgO.NH_4O.AsO_5 + HO$. Exposure to a higher temperature occasions loss of arsenic.

If the liquid contains arsenious acid, that compound may be converted into arsenic acid by mixing the solution with hydrochloric acid, and adding chlorate of potash by small quantities. The vessel must be left in a moderately warm place till the odour of free chlorine has entirely disappeared. Aqua regia may also be used to effect the oxidation, but it is less convenient. In either case, the liquid must be considerably diluted with water, otherwise part of the arsenic will be converted into chloride, and volatilised. It is best, perhaps, to perform the oxidation in a capacious retort having a receiver adapted to it.

Arsenious acid may also be estimated by its action on terchloride of gold. The arsenious acid is thereby converted into arsenic acid, and gold is precipitated in the metallic state. The quantity of gold thus reduced gives the quantity of arsenious acid present:

$$2AuCl_3 + 6HO + 3AsO_3 = 2Au + 6HCl + 3AsO_5.$$

The gold solution used for the purpose is the sodio-chloride, or ammonio-chloride of gold. It must be free from nitric acid; but the presence of hydrochloric acid, even in large excess, does not interfere with the action. The liquid, after the addition of the arsenic solution, must be left to itself for a considerable time to enable the gold to settle down completely.

When arsenic and arsenious acids exist together in solution

the former may be precipitated as ammonio-magnesian arseniate (a considerable quantity of sal-ammoniac being added to prevent the simultaneous precipitation of the arsenious acid); the arsenious acid converted into arsenic acid by oxidation with chlorate of potash and hydrochloric acid, and then precipitated in a similar manner; or the arsenious acid may be estimated by chloride of gold, as last described.

The separation of arsenic in solution from the alkalies, earths, and those metals which are not precipitated from their acid solutions by hydrosulphuric acid, is effected by passing a stream of that gas through the acid liquid for a considerable time, then leaving it to stand, and heating it gently to ensure the complete precipitation of the sulphide of arsenic. If the arsenic is in the form of arsenic acid, that compound must be previously reduced to arsenious acid by means of sulphurous acid. The tersulphide of arsenic is collected on a weighed filter, thoroughly washed, and dried at a moderate heat. If quite pure, it may be weighed with the filter, and the quantity of arsenic thereby directly determined. But as it almost always contains an excess of sulphur, it is better to take a weighed quantity of it from the filter, oxidise it in a capacious flask by means of dilute hydrochloric acid and chlorate of potash, continuing the operation till the greater part of the sulphur is converted into sulphuric acid, and the remainder collects at the bottom of the liquid in a compact yellow globule; then decant the liquid, wash the globule of sulphur, and weigh it; and, finally, estimate the quantity of sulphur in the solution by precipitation with chloride of barium, adding the quantity thus found to the weight of the globule. The proportion of sulphur in the precipitated sulphide of arsenic being thus ascertained, the amount of arsenic is easily calculated.

From *cadmium, copper,* and *lead,* arsenic may be separated by means of sulphide of ammonium. The filtered ammoniacal solution is then treated with excess of hydrochloric or acetic

acid to throw down the sulphide of arsenic, and the precipitate treated in the manner just described.

The separation of arsenic from *tin* is attended with considerable difficulty. One of the best methods is to convert the two metals into sulphides, and separate them, after drying and weighing the whole, by ignition in a stream of hydrosulphuric acid gas. The mixed sulphides are introduced into a weighed glass bulb, having a tube attached to it on each side. One of these tubes, the exit-tube, must be at least a quarter of an inch in diameter, to prevent stoppage, and bent downwards so as to dip into a flask containing ammonia. The whole is then weighed, hydrosulphuric acid gas passed through the apparatus, and the bulb heated till the whole of the sulphide of arsenic is sublimed. Part of the sulphide of arsenic passes into the ammoniacal liquid, by which it is dissolved, and the rest sublimes in the wide tube. When the operation is ended, and the apparatus has cooled, the wide tube is cut off at a short distance from the bulb, then broken, and the pieces digested in caustic potash to dissolve out the sulphide of arsenic. The solution thus obtained is added to the ammoniacal liquid in the flask; the sulphide of arsenic precipitated by hydrochloric acid, oxidised without previous filtration with hydrochloric acid and chlorate of potash; and the resulting arsenic acid precipitated by ammonia and sulphate of magnesia. The sulphide of tin remaining in the bulb is converted into stannic oxide by treating it with strong nitric acid.

When arsenic is combined with other metals in the form of an alloy, the whole may be dissolved or oxidised by means of aqua regia, or, better, with hydrochloric acid and chlorate of potash, and the arsenic separated by one of the preceding methods. In the case of tin, however, it is best to fuse the alloy in thin laminæ with five times its weight of carbonate of soda and an equal quantity of sulphur, whereby a mixture of sulpharseniate and sulphostannate of soda is obtained, which

dissolves completely in hot water. The sulphides of tin and arsenic may then be precipitated by hydrochloric acid, and separated as above.*

SECTION II.

ANTIMONY.

Eq. 120·24 *or* 1503†; Sb (*stibium*).

This metal was well known to the alchemists, and is one of the metals the preparations of which were first introduced into medicine. Its sulphide is not an uncommon mineral, and is the source from which the metal and its compounds are always derived.

The sulphide of antimony is easily reduced to the metallic state by mixing together 4 parts of that substance, 3 parts of crude tartar, and $1\frac{1}{2}$ parts of nitre, and projecting the mixture by small quantities at a time into a red hot crucible. The sulphide is also sometimes reduced by fusion with small iron nails, which combine with the sulphur and disengage the antimony. Or it may be obtained in a state of greater purity by strongly igniting in a crucible a quantity of the potash-tartrate of antimony, and placing the resulting metallic mass in water to remove any potassium it may have acquired.

Antimony is a white and brilliant metal, generally possessing a highly lamellated structure. It is easily obtained

* For a full account of the methods of estimating arsenic and separating it from other metals, *vide* H. Rose, "Handbuch der analytischen Chemie," 1851, ii. 381.

† The number 129, given by Berzelius for the equivalent of antimony, and hitherto generally adopted, appears from recent experiments by Schneider (Pogg. Ann. xcviii. 293) and by H. Rose (Berl. Akad. Ber. 1856, p. 229) to be much too high. Schneider, by reducing the tersulphide of antimony with hydrogen, finds the equivalent to be 120·24; and Rose, by decomposing the terchloride with hydrosulphuric acid, and precipitating the chlorine with nitrate of silver, finds the number 120·69.

in rhombohedral crystals of the same form as arsenic and tellurium. Its density is from 6·702 to 6·86. It undergoes no change in the air. The point of fusion of antimony is estimated at 797°; it may be distilled at a white heat. This metal burns in air at a red heat, and produces copious fumes of oxide of antimony.

Antimony combines in three proportions with oxygen, forming oxide of antimony and antimonic acid, SbO_3 and SbO_5, which correspond respectively with arsenious and arsenic acids; and antimonious acid, SbO_4, which is probably an intermediate or compound oxide, analogous to the black oxide of iron.

Teroxide of antimony, Antimonic oxide, Antimonious acid, SbO_3, 144·24 or 1803.—This oxide may be obtained by dissolving the sulphide, finely pounded and in the condition in which it is known as prepared sulphide of antimony, in four times its weight of concentrated hydrochloric acid. Pure hydrosulphuric acid goes off, and the antimony is converted into terchloride:

$$SbS_3 + 3HCl = SbCl_3 + 3HS.$$

The clear solution may be poured off, and precipitated at the boiling heat by a solution of carbonate of potash added in excess, the carbonic acid, which does not combine with oxide of antimony, escaping as gas. Teroxide of antimony, so prepared, is anhydrous, but is slightly soluble in water: it is white, but assumes a yellow tint when heated. It is fusible at a red heat, and sublimes at a high temperature in a close vessel, where it cannot pass into a higher state of oxidation. The brilliant crystalline needles which condense about antimony in a state of combustion likewise consist of this oxide. They possess the unusual prismatic form of arsenious acid observed by Wöhler. Oxide of antimony also crystallises as frequently in regular octohedrons, the other form of arsenious acid. It occurs in the prismatic form as a rare mineral, whose density is 5·227.

When a solution of potash is poured upon the bulky hydrate of teroxide of antimony, which is precipitated from the chloride by water, a portion of the oxide is dissolved, but the greater part loses its water, and is reduced in a few seconds to a fine greyish, crystalline powder, which is a neutral combination of teroxide of antimony with potash. Teroxide of antimony also combines with acids, forming the *salts of antimony*, or *antimonic salts*.

The solutions of these salts give with *hydrosulphuric acid* a brick-red precipitate of tersulphide of antimony, easily soluble in sulphide of ammonium, and reprecipitated by acids. This precipitate dissolves in strong boiling hydrochloric acid, forming the terchloride, which when thrown into water yields a precipitate of the oxychloride. This reaction with hydrosulphuric acid distinguishes antimony from all other metals.* *Zinc* or *iron* precipitates antimony from its solutions in the form of a black powder, which, when fused on charcoal before the blow-pipe, yields a brittle button of the metal. According to Dr. Odling†, antimony is also precipitated by *copper*, in the form of a brilliant metallic film, which may be dissolved off the copper by a solution of permanganate of potash, yielding a solution which will give the characteristic red precipitate with hydrosulphuric acid. This reaction affords a ready method of separating antimony from liquids containing organic matter,—as in medico-legal inquiries. All compounds of antimony fused upon charcoal with *carbonate of soda* or *cyanide of potassium*, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of antimonic oxide. The reduction with cyanide of potassium may also be performed in a porcelain crucible, without charcoal. A solution of *terchloride of gold* added to

* For the reactions of antimonic salts with alkalies, see *terchloride of antimony* and *tartar-emetic*.

† Guy's Hospital Reports, [3.] ii. 249.

the solution of a salt of teroxide of antimony, forms a yellow precipitate of metallic gold, the oxide of antimony being at the same time converted into antimonic acid, which compound is precipitated as a white powder, together with the gold, unless the solution contains a very large excess of hydrochloric acid. In a solution of oxide of antimony in potash, terchloride of gold produces a black precipitate, which is not altered by heating. This reaction is extremely delicate.

Tersulphide of antimony, SbS_3, 168·24 or 2103.—The common ore of antimony is a tersulphide, SbS_3, corresponding with the preceding oxide of antimony. It is rarely free from sulphide of arsenic, which thus often enters into the antimonial preparations derived from the sulphide of antimony, but into tartar-emetic less frequently than the others. The same sulphide is formed when salts of the oxide of antimony, such as tartar-emetic, are precipitated by hydrosulphuric acid; but it is then of an orange-red colour. When the precipitated sulphide is dried, it loses water and becomes anhydrous, still remaining of a dull orange colour; but when heated more strongly, it shrinks at a particular temperature, and assumes the black colour and metallic lustre of the native sulphide. This sulphide is also obtained of a dark brown colour by boiling the prepared sulphide of antimony in a solution of carbonate of potash, and allowing the solution to cool; by fusing $2\frac{2}{3}$ parts of the prepared sulphide with 1 part of carbonate of potash; or dissolving it in a boiling solution of caustic potash, and afterwards adding an acid. The last preparation is known as *Kermes mineral*. It has a much duller colour than the precipitated sulphide, but differs from it only in containing small quantities of oxide and pentasulphide of antimony, together with an alkaline sulphide which cannot be removed by washing (Berzelius). When the cooled mother-liquor from which kermes is deposited is mixed with hydrochloric acid, a precipitate is obtained, consisting, like the kermes, of SbS_3 mixed with SbO_3 and SbS_5, but of a redder

colour. It is sometimes called the *golden sulphuret of antimony*.

When the sulphide of antimony is oxidated at a red heat, much sulphur is burned off, and an impure oxide of antimony remains. This matter forms, when fused, the *glass of antimony*, which contains a considerable quantity of undecomposed sulphide. The glass, reduced to powder, is boiled with bitartrate of potash as a source of oxide of antimony, in the pharmaceutical preparation of tartar-emetic. The oxide of antimony is dissolved out from the glass by acids, and a substance is left which is called *saffron of antimony*. This last is a definite compound of oxide and sulphide of antimony, $SbO_3 . 2SbS_3$, which also occurs as a mineral—namely, red antimony ore.

Terchloride of antimony, $SbCl_3$, is obtained by distilling either metallic antimony or the tersulphide of antimony with corrosive sublimate. When heated it flows like an oil, and becomes a crystalline mass on cooling. It is a powerful cautery. This salt deliquesces in air, and becomes turbid, owing to the deposition of a subsalt. A concentrated solution of chloride of antimony is also obtained by dissolving the sulphide of antimony in hydrochloric acid. When this solution is thrown into water, it gives a white bulky precipitate, which after a time resolves itself into groups of small crystals, having usually a fawn colour; it was formerly called the *powder of Algaroth*. These small crystals are an oxychloride of antimony, which, according to the analyses of Johnston and Malaguti, contains $2SbCl_3 . 9SbO_3$.

A solution of terchloride of antimony, to which water is added, and then a sufficient quantity of hydrochloric acid to redissolve the precipitate thereby produced, gives with *potash* a white precipitate of the hydrated teroxide, soluble in a very large excess of the alkali. *Ammonia* forms the same precipitate insoluble in excess. *Carbonate of potash*, or *soda*, produces also a white precipitate of the hydrated teroxide, which

is soluble in excess, especially of the potash-salt, but reappears after a while. These reactions are greatly modified by the presence of fixed organic acids, especially of tartaric acid. In such a case, water forms no precipitate, ammonia but a slight one and after some time only, and the precipitate formed by potash dissolves easily in excess of the alkali. (See *Tartar-emetic.*)

Terfluoride of antimony, SbF_3, is obtained, by treating the teroxide with strong hydrofluoric acid, in colourless crystals which dissolve in water without decomposition. It unites with fluoride of potassium, forming the compound $3KF . SbF_3$ and similarly with fluoride of sodium and fluoride of ammonium.

Sulphate of antimony, $SbO_3 . 3SO_3$, is obtained, by boiling metallic antimony with concentrated sulphuric acid, as a white saline mass, which is decomposed by water.

Oxalate of potash and antimony, $KO . C_2O_3 + SbO_3 . 3C_2O_3$. —This is a double crystallisable salt of antimony, which, like the tartrate of potash and antimony, may be dissolved in water without decomposition. It is prepared by saturating binoxalate of potash with oxide of antimony. It is soluble at 48° in ten times its weight of water (Lassaigne). According to Bussy, when binoxalate of potash is digested upon oxide of antimony in excess, two salts are formed, one in oblique prisms, and another less soluble, in intricate small crystals; but neither is very stable. The former is decomposed by a large quantity of water: its analysis gave $3(KO . C_2O_3) + SbO_3 . 3C_2O_3 + 6HO$.*

Tartrate of potash and antimony, $KO . SbO_3 + C_8H_4O_{10}.2HO$. —This salt, the tartar-emetic or potash tartrate of antimony of pharmacy, is prepared by neutralising bitartrate of potash with oxide of antimony; the oxide obtained by decomposing the chloride or sulphate of antimony with water answers best for the purpose. A quantity of oxide of anti-

* J. Pharm. 1838, p. 509.

mony may be boiled with three or four times its weight of water, and bitartrate of potash added in small quantities till the oxide is entirely dissolved. The filtered solution yields the salt, on cooling, in large transparent crystals, the form of which is an octohedron with a rhombic base; they become white in the air, and lose their water of crystallisation. They are soluble in 14 times their weight of cold water, and in 1·88 parts of boiling water, but not in alcohol. The mother-liquor of these crystals becomes a syrupy liquid, and dries up into a gummy mass without crystallising, when oxide of antimony has been dissolved in excess by the acid tartrate in preparing the salt. *Potash* added to a solution of the salt throws down the teroxide of antimony, but the precipitate is easily soluble in excess of potash. *Ammonia* forms no precipitate at first, and but a slight one after standing. *Alkaline carbonates* form a precipitate of the teroxide insoluble in excess of the reagent. With *hydrosulphuric acid*, the reaction is the same as with other salts of antimony. (See p. 224.) Salts of the earths and basic metallic oxides, such as *baryta* and *oxide of silver*, throw down from its solution a compound of the tartrate of antimony with tartrate of baryta, tartrate of silver, &c. (Wallquist.) Strong acids decompose the salt, and produce a precipitate which is a mixture of bitartrate of potash with oxide of antimony, or with a subsalt of that oxide.

This salt was formerly described as a double tartrate of potash and antimony, or, abstracting its water of crystallisation, which is differently stated at 2 and 3 equivalents, as $KO.(C_4H_2O_5)+SbO_3.(C_4H_2O_5)$. When the atomic weight of tartaric acid is doubled, and it is represented as a bibasic acid, the formula for dry tartar-emetic becomes $KO.SbO_3.(C_8H_4O_{10})$. In comparing the last formula with that of bitartrate of potash, represented also as a bibasic salt, $KO.HO.(C_8H_4O_{10})$, it is observed that 1 eq. of oxide of antimony takes the place of 1 eq. of water as base, although the

former contains 3 eq. of oxygen, and the latter only one. Tartrate of potash and antimony is, in this respect, an anomalous salt. Another equally remarkable fact respecting this salt has been observed by M. Dumas, namely, that 2 eq. of water are separated from the anhydrous salt at 428°, leaving a substance of which the elements are $C_8H_2O_{12}$ SbK. The first part of this formula $C_8H_2O_{12}$, M. Dumas looks upon as a quadribasic salt-radical, existing in the tartrates, which in hydrated tartaric acid is united with 4H, in bitartrate of potash with 3H + K, and in tartrate of antimony and potash with Sb + K. Here Sb is found equivalent to and capable of replacing 3H. Tartrate of antimony and potash might, therefore, be represented by $KSb(C_8H_2O_{12}) + 2HO$ + water of crystallisation. If SbO_2 be regarded as a radical capable of replacing 1 eq. of hydrogen (similar to uranyl, U_2O_2, the hypothetical radical of the uranic salts), the formula of tartar-emetic dried at 212° may be written as $C_8H_4K(SbO_2)O_{12}$, and that of the salt dried between 392° and 428°, as $C_8H_2K(SbO_2)O_{10}$.

Antimonic acid, SbO_5,160·24 *or* 2003.—This compound is obtained in the hydrated state: 1. By treating antimony with nitric acid, or with aqua-regia containing excess of nitric acid. 2. By decomposing pentachloride of antimony with water. 3. By precipitating a solution of antimoniate of potash with an acid.

The hydrated acid obtained by either of these methods gives off its water at a moderate heat, and yields *anhydrous antimonic acid* in the form of a yellowish powder, which is tasteless, insoluble in water, decomposes alkaline carbonates, and, when heated to redness, gives off oxygen, and is converted into antimoniate of antimonic oxide, $SbO_3 . SbO_5$.

The hydrates obtained by the three methods above described are by no means identical. The acid in the first is monobasic, whereas in the other two it is bibasic. The bibasic acid is distinguished by the name of *metantimonic acid*,

while the monobasic acid is called simply *antimonic acid* (Fremy).

Antimonic acid forms neutral or normal salts, containing $MO.SbO_5$, and acid salts whose formula is $MO.(SbO_5)_2$. Metantimonic acid forms neutral salts containing $(MO)_2.SbO_5$, and acid salts containing $(MO)_2.(SbO_5)_2$, or $MO.SbO_5$, so that the acid metantimoniates are isomeric or polymeric with the neutral antimoniates. An acid metantimoniate easily changes into a neutral antimoniate. The metantimoniates of potash, soda, and ammonia are crystalline; the antimoniates of the same bases are gelatinous and uncrystallisable. The soluble acid metantimoniates form a crystalline precipitate with salts of soda; the soluble antimoniates do not form any such precipitate (Fremy).

Antimoniates of potash.—The neutral salt, $KO.SbO_5.5HO$, is obtained by fusing 1 part of antimony with 4 parts of nitre, digesting the fused mass in tepid water to remove nitrate and nitrite of potash, and boiling the residue for an hour or two with water. The white insoluble mass of anhydrous antimoniate is thereby transformed into a hydrate containing 5 eq. water, which is soluble. The solution when evaporated leaves this hydrate in the form of a gummy uncrystallisable mass, which gives off 2 eq. of water at 320°, and the whole at a higher temperature.

Acid antimoniate of potash, $KO.(SbO_5)_2$ is obtained by passing carbonic acid gas through a solution of the neutral antimoniate. It is white, crystalline, perfectly insoluble in water, and is converted into the neutral salt when heated with excess of potash. This salt is the *antimonium diaphoreticum lavatum* of the pharmacopœias (Fremy).

Neutral metantimoniate of potash, $2KO.SbO_5$, is prepared by fusing antimonic acid or neutral antimoniate of potash with a large excess of potash. The fused mass dissolves in a small quantity of water, and the solution evaporated in vacuo yields crystals of the neutral metantimoniate. This salt

dissolves freely and without decomposition in warm water containing excess of potash; but cold water or alcohol decomposes it into potash and the acid metantimoniate. Hence the aqueous solution of this salt gives a precipitate, after a while, with salts of soda (Fremy).

Acid metantimoniate of potash, $KO . SbO_5 + 7HO$, sometimes called *granular antimoniate of potash.*—This salt is used as a test for soda. To obtain it, the neutral antimoniate is first prepared and dissolved in the manner above described; the solution filtered to separate any acid antimoniate that may remain undissolved; then evaporated to a syrup in a silver vessel; and hydrate of potash added in lumps to convert the antimoniate into metantimoniate. The evaporation is continued till the liquid begins to crystallise, which is ascertained by taking out a drop now and then upon a glass rod, and the liquid is left to cool. A crystalline mass is thus obtained, consisting of neutral and acid metantimoniate of potash; the alkaline liquor is then decanted, and the salt dried upon filtering paper or unglazed porcelain (Fremy). This salt may also be prepared by treating terchloride of antimony with an excess of potash sufficient to redissolve the precipitate first formed, and adding permanganate of potash till the solution acquires a faint rose colour. The liquid, filtered and evaporated, yields crystals of the granular metantimoniate (Reynoso). This salt is sparingly soluble in cold water, but dissolves readily in water between 113° and 122°. When boiled with water for a few minutes, or kept in contact with water for some time, it is converted into the neutral antimoniate. It must therefore be preserved in the solid state, and dissolved just before it is required for use. A small quantity of it is then treated with about twice its weight of cold water to remove excess of potash, and convert any neutral metantimoniate into the acid salt; the liquid decanted; the remaining salt rapidly washed three or four times with cold water; then left in contact with water for a

few minutes, and the liquid filtered. On adding to the solution thus obtained, a small quantity of any soda-salt, a crystalline precipitate is formed, consisting of *acid metantimoniate of soda*, $NaO . SbO_5 + 7HO$. This reaction is apparent in a solution containing only 1 part of soda in 300. In strong solutions of soda, the precipitate appears immediately, but in dilute solutions only after a while, the crystals being deposited on the sides of the vessel. An excess of potash in the reagent also retards the precipitation (Fremy*).

Antimoniates of ammonia.—When the metantimonic acid, obtained by decomposing pentachloride of antimony with water, is treated with ammonia, part of it dissolves, and a solution is formed containing *neutral metantimoniate of ammonia.* A few drops of alcohol added to the solution, throw down a precipitate consisting of *acid metantimoniate of ammonia*, $NH_4O . SbO_5 + 6HO$. This salt is slightly soluble, and its solution precipitates soda-salts. It changes spontaneously in a few days, even when kept in a close vessel, into neutral *antimoniate* of ammonia, which is completely insoluble in water. The same change is instantly produced in it by heat (Fremy).

Antimoniate of lead, $PbO . SbO_5$, may be obtained as a yellow powder by fusing antimonic acid with oxide of lead, or as a white hydrate by precipitation: the hydrate gives off its water when heated, and turns yellow. This salt is used as a pigment under the denomination of *Naples yellow*.

Antimoniate of antimony, $SbO_3 . SbO_5$. or SbO_4, is obtained by the action of heat upon antimonic acid, by roasting the

* Traité de Chimie Générale, par Pelouze et Fremy, 2me. ed. t. 3. pp. 151. 157. According to Heffter (Pogg. Ann. lxxxvi. 418.), the granular antimoniate of potash is $KO . HO + 12(KO . SbO_5 + 7HO)$; the precipitated soda-salt is similarly constituted; and by treating the solution of this salt in boiling water with salts of the earths and metallic oxides, precipitates are obtained, also of similar composition, or differing only in the water which they contain. Heffter's formulæ were calculated according to the old equivalent of antimony, 129; but Schneider has shown that, on re-calculating the analyses with the lower equivalent 120·24, the numbers of the equivalents of base and acid come out equal.

teroxide or tersulphide, or by treating powdered antimony with excess of nitric acid. It is white, infusible, and unalterable by heat; slightly soluble in water. It was formerly regarded as a distinct acid, SbO_4, and called *antimonious acid;* but it does not form salts; and, when boiled with bitartrate of potash, it is resolved into cream of tartar, which dissolves, and a residue of antimonic acid.

Pentasulphide of antimony, Sulphantimonic acid, SbO_5, is obtained by passing hydrosulphuric acid gas into an acid solution of pentachloride of antimony, or into the solution of an alkaline antimoniate. It has an orange-colour much less red than the tersulphide; it is the *golden sulphuret of antimony* of several pharmacopœias. It combines with basic metallic sulphides, forming the *sulphantimoniates.* The *sodium-salt,* $3NaS . SbS_5$, which is sometimes used in medicine, is obtained by mixing 18 parts of finely pounded tersulphide of antimony, 12 parts of dry carbonate of soda, 13 parts of lime, and $3\frac{1}{4}$ parts of sulphur; triturating the mixture for about half an hour; leaving it for two or three days in a flask filled with water, and shaking it from time to time; then filtering and evaporating, first over the open fire, afterwards in vacuo. The salt is thus obtained in large regular tetrahedrons of a pale yellow colour. It is very soluble in water, and is decomposed by acids, which throw down hydrated pentasulphide of antimony.

Pentachloride of antimony, $SbCl_5$, is obtained by heating metallic antimony in a current of dry chlorine, and distilling the product in a dry retort, rejecting the first portions of the distillate, which contain excess of chlorine. It is a yellowish, very volatile liquid, which emits suffocating vapours. Water first converts it into a crystalline hydrate, and then decomposes it, forming antimonic acid: $SbCl_5 + 5HO = SbO_5 + 5HCl$. It absorbs ammonia and phosphuretted hydrogen, forming red-brown solid compounds. It absorbs olefiant gas as readily as chlorine, and forms Dutch liquid. It likewise absorbs hydrosulphuric acid gas at ordinary temperatures, forming a

white crystalline mass, consisting of *chlorosulphide of antimony*, $SbCl_3S_2$, exactly analogous to chlorosulphide of phosphorus PCl_3S_2. Pentasulphide of antimony, treated with dry chlorine aided by heat, forms a white pulverulent compound, containing $SbCl_8S_3$, or $SbCl_5.3SCl$; this compound is decomposed at 572° (300° C.) into chlorine, chloride of sulphur, and terchloride of antimony. Pentachloride of antimony combines with hydrocyanic acid, forming a white, crystalline, volatile compound, composed of $SbCl_5.3HCy$. It also combines with chloride of cyanogen.

Antimoniuretted hydrogen.—This compound is obtained by dissolving an alloy of zinc and antimony in hydrochloric or dilute sulphuric acid, or by dissolving zinc in either of these dilute acids containing oxide or chloride of antimony, tartar-emetic, &c. The gas, however, always contains more or less free hydrogen. Its comparative purity may be tested by means of a solution of nitrate of silver, which absorbs the antimoniuretted hydrogen, and leaves the free hydrogen. An alloy of 2 parts zinc and 1 part antimony yields the purest gas; an alloy containing a larger proportion of antimony gives more free hydrogen; and an alloy of equal parts of the two metals yields scarcely anything but free hydrogen. As the compound has never been obtained in a state of purity, its composition has not been correctly ascertained, but it is probably SbH_3.

Antimoniuretted hydrogen is a colourless gas, and when free from arsenic, quite inodorous. It is insoluble in water, and in alkaline liquids; with solutions of silver or mercury it forms precipitates containing silver or mercury, together with antimony. When burned from a jet, it deposits, on a plate of porcelain, metallic spots, greatly resembling those of arsenic, but differing from the latter in possessing less lustre and in not being soluble in hypochlorite of soda. They may also be dissolved in aqua-regia or in permanganate of potash (p. 224), and the solution will give the characteristic orange

precipitate with hydrosulphuric acid. A metallic deposit may also be obtained by heating a glass tube through which the gas is passed; and this deposit, when sublimed, will not exhibit the characters of arsenic (p. 216).

Alloys of antimony with *potassium* or *sodium* may be obtained by igniting metallic antimony, or its oxide or sulphide, with an organic salt of potash or soda. Thus, when 5 parts of crude tartar and 4 parts of antimony are slowly heated in a covered crucible till the mixture becomes charred, then heated to whiteness for an hour, and left to cool, a crystalline regulus is obtained containing 12 per cent. of potassium. This alloy decomposes water rapidly, and oxidises slowly in the air when in the compact state, but becomes heated and takes fire when rubbed to powder.

A mixture of 7 parts of antimony and 3 parts of *iron*, heated to whiteness in a crucible lined with charcoal, forms a white, very hard, slightly magnetic alloy, which gives sparks when filed. It is always formed when sulphide of antimony is reduced by iron in excess.

With *zinc*, antimony forms alloys of definite crystalline character. A fused mixture of the two metals, containing from 43 to 70 per cent. of zinc, deposits by partial cooling, silver-white rhombic prisms, containing from 43 to 64 per cent. of zinc. The alloy containing exactly 43 per cent. of zinc, appears to be a definite compound, *stibiotrizincyl*, $SbZn_3$. Mixtures containing from 33 to 20 per cent. of zinc deposit rhombic crystals containing from 35 to 21 per cent. of zinc. The alloy containing exactly 33 per cent. is *stibiobizincyl*, $SbZn_2$. These alloys, especially $SbZn_3$, decompose water with evolution of hydrogen at the boiling heat, and very rapidly under the influence of acids (J. P. Cooke *).

Type-metal, is an alloy of antimony and lead, usually containing 76 per cent. of lead, which corresponds nearly with the formula Pb_2Sb.

* Sill. Am. J. [2.] xviii. 229; xx. 222.

ESTIMATION OF ANTIMONY, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Antimony cannot be estimated in the form of antimonious or antimonic acid, because we can never be sure of the purity of those bodies. The best mode of proceeding is to precipitate it by hydrosulphuric acid, collect the sulphide of antimony on a weighed filter, and, after ascertaining the total quantity of the precipitate, estimate the proportion of sulphur in it in the manner already described with reference to sulphide of arsenic (p. 219). Or the sulphide of antimony may be decomposed by heating it in a current of hydrogen gas, whereupon hydrosulphuric acid and sulphur-vapour escape, and metallic antimony remains behind. For this purpose, a weighed portion of the sulphide is placed in a small porcelain crucible having a hole in its cover, through which a tube passes to convey the hydrogen. The temperature is gradually raised, and the process continued till the weight of the crucible no longer varies. The reduction may also be performed in a bulb-tube.

When antimonious and antimonic acids occur together in solution, the total quantity of antimony may be ascertained by treating one portion of the liquid in the manner just described, and the quantity existing as antimonious acid may be determined in another portion by means of terchloride of gold, 2 eq. of precipitated gold corresponding to 3 eq. of antimonious acid:

$$2AuCl_3 + 6HO + 3SbO_3 = 2Au + 6HCl + 3SbO_5.$$

The separation of antimony from the *alkalies* and *earths*, and from those metals which are not precipitated from their acid solutions by hydrosulphuric acid, is effected by means of that reagent.

To separate antimony from *cadmium, copper,* and *lead,* the

solution, after being neutralised with ammonia, is mixed with sulphide of ammonium containing excess of sulphur. The sulphide of antimony then dissolves, the other sulphides remaining undissolved; and on mixing the filtrate with acetic acid (hydrochloric acid might redissolve a portion of the precipitate, especially as the liquid becomes heated), the sulphide of antimony is reprecipitated, and may be treated as above.

When antimony is combined with any of the preceding metals in the form of an alloy, it may be separated by treating the alloy with nitric acid, whereby the other metals are dissolved, and the antimony converted into insoluble antimonic acid. This method is, however, not rigidly exact; for the nitric acid dissolves a small portion of the antimony.

Separation of antimony from arsenic and tin.—The separation of these metals is attended with considerable difficulty. The best mode of effecting it is to convert them into arseniate, stannate, and antimoniate of soda, and treat the mixture with dilute alcohol, which dissolves the arseniate and stannate of soda, and leaves the antimoniate undissolved.

If the three metals exist together in solution, they must be precipitated as sulphides by hydrosulphuric acid, and the precipitate treated by one of the following methods: —

(1.) The precipitated sulphides are fused in a silver crucible with a mixture of hydrate of soda and nitre: or, better, they are oxidised by heating them with strong nitric acid; the solution, together with the insoluble stannic and antimonic acids, mixed with excess of caustic soda, and evaporated to a small bulk; then transferred to a silver crucible, evaporated to dryness, and kept for some time in a state of red hot fusion. The fused mass, consisting of arseniate, stannate, and antimoniate of soda, is disintegrated by digestion in warm water; the contents of the crucible transferred to a beaker-glass; and the crucible well rinsed out with a *measured* quantity of water. The greater part of the arseniate and stannate of soda then dissolves, while the anti-

moniate remains undissolved. But to effect complete separation, a quantity of alcohol of sp. gr. 0·833 is added, equal in bulk to one-third of the water used; the mixture left to stand for 24 hours and frequently stirred; and the antimoniate of soda, which has then completely settled down, is collected on a filter and washed, first, with a mixture of 1 volume of the same alcohol to 3 vols. of water, then with 1 vol. alcohol to 2 vols. water; next, with a mixture of equal measures of water and alcohol; and, lastly, with 3 vols. alcohol to 1 vol. water (H. Rose).*

(2.) The precipitated sulphides of the three metals are dissolved in a mixture of sulphide of sodium and caustic soda, and the liquid mixed with a solution of hypochlorite of soda. The sulphides are thereby oxidised and converted into arsenic, stannic, and antimonic acids, which combine with the soda, and may be separated by treatment with dilute alcohol, and washing, as in Rose's process. This method is due to Dr. Williamson; it is easier of execution than the former, as the fused mixture of the soda-salts is very hard, and difficult to disintegrate by water.

The antimoniate of soda, separated by either of these processes, is digested in a mixture of hydrochloric and tartaric acids, which dissolves it completely; the antimony then precipitated by hydrosulphuric acid; and its quantity estimated in the manner already described (p. 235).

The filtrate containing the arseniate and stannate of soda is supersaturated with hydrochloric acid, which throws down a bulky precipitate of arseniate of stannic oxide; hydrosulphuric acid gas passed through the liquid till the white precipitate is completely converted into a brown mixture of the sulphides of tin and arsenic; the whole left to stand till the odour of hydrosulphuric acid is no longer perceptible; the precipitate collected on a weighed filter; and the filtrate

* Handb. d. anal. Chem. 1851. ii. 429.

heated for some time to expel the greater part of the alcohol; then mixed with sulphurous acid, and again treated with hydrosulphuric acid, whereby a small quantity of sulphide of arsenic is generally precipitated. This quantity of sulphide of arsenic being quite free from tin, need not be added to the mixed sulphides on the filter.

These mixed sulphides are dried at 212°, their total weight determined, and a known quantity heated in a stream of hydrosulphuric acid gas in the manner described at page 220. The residual sulphide of tin is then converted into stannic oxide, and the sublimed sulphide of arsenic, together with the small quantity separately precipitated, is converted into arsenic acid by treatment with hydrochloric acid and chlorate of potash, and the arsenic precipitated as ammonio-magnesian arseniate (H. Rose).

If the three metals are in the state of solid oxides, the mixture may be dissolved in hydrochloric acid, with addition of tartaric acid, and the metals precipitated as sulphides as before. If the metals are mixed in the form of an alloy, they may be dissolved in aqua-regia, the solution mixed with tartaric acid, then diluted, and precipitated in the same manner.

The method just described may, of course, be applied to the separation of antimony from tin or from arsenic alone. In these cases, however, simpler methods may often be advantageously adopted.

Separation of antimony from tin—When these two metals exist together in solution, and the sum of their weights is known, the separation may be effected, and the weights of the two determined, by immersing in the solution a piece of pure tin, which precipitates the antimony in the form of a black powder. To render the precipitation complete, a gentle heat must be applied, and the solution must contain excess of acid. The antimony is collected on a weighed filter, dried at a gentle heat, and weighed. If the sum of the weights is not previously known, the metals must be precipitated together

by zinc from a known quantity of the solution, and the antimony precipitated by tin from another portion. When the two metals exist together in an alloy, a portion of the alloy must be weighed, then dissolved in aqua-regia, and the solution mixed with tartaric acid, diluted with water, and treated as above.

Another method of separation is to precipitate the two metals with zinc, and treat the precipitate with strong hydrochloric acid without previously decanting the solution of chloride of zinc. The tin then dissolves, while the antimony remains undissolved, the presence of the chloride of zinc diminishing its tendency to dissolve in the acid. The tin may afterwards be precipitated by hydrosulphuric acid, and the sulphide converted into stannic oxide, by treating it with strong nitric acid (Levol).*

Separation of antimony from arsenic.—When these two metals are associated in the metallic state, they may be completely separated by heating the alloy in a stream of carbonic acid, the arsenic then volatilising, and the antimony remaining. Antimony is, however, the only metal from which arsenic can be completely separated in this manner; hence, if the alloy contains any other metal, some of the arsenic will be retained, and the method is no longer applicable.

When this is the case, the alloy may be dissolved in aqua regia, or in hydrochloric acid to which chlorate of potash is gradually added; the solution diluted with water after addition of tartaric acid; then mixed with a considerable quantity of chloride of ammonium and excess of ammonia; and the arsenic precipitated as ammonio-magnesian arseniate by addition of sulphate of magnesia. The antimony may then be precipitated from the filtrate by hydrosulphuric acid.

* Ann. Ch. Phys. [3.] xiii. 125.

SECTION III.

BISMUTH.

Eq. 213, *or* 2662·5; Bi.

Bismuth is generally found in the metallic state, disseminated in quartz-rock; but occurs also as an oxide, carbonate, and sulphide, either alone or associated with other metals; also in combination with tellurium. Native bismuth is, however, the only mineral which occurs in sufficient abundance for the economical extraction of the metal. The process of extraction as performed in Saxony, whence all the bismuth of commerce is obtained, is very simple, the mineral being merely heated in close vessels, so as to melt the bismuth, and thereby separate it from the gangue or accompanying rock. The fusion is performed in iron tubes, laid in an inclined position, in a furnace. (*Fig.* 11.) The ore is introduced at the upper end, *d*, which is then plugged. The other end, *b*, is closed with an iron plate having an aperture, *o*, through which the melted metal runs into earthen pots, *a*, heated by a few coals placed in the space, *K*, below, so as to keep the metal in the melted state. It is then ladled out and run into moulds. The crude metal thus obtained is afterwards fused with 1-10th of its weight of nitre, to free it from sulphur, arsenic, and certain foreign metals.

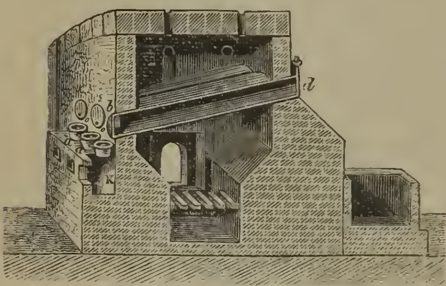


Fig. 11.

Commercial bismuth, however, is still somewhat impure. To free it completely from other metals, it is dissolved in

nitric acid, the clear liquid decanted and mixed with water, which throws down a subnitrate of bismuth; and this compound is reduced at a moderate heat, either with black flux, or in a crucible lined with charcoal.

Bismuth crystallises in octohedrons and cubes. It may be obtained in very beautiful crystals, by fusing several pounds of the ordinary metal in a crucible or iron ladle, adding nitre from time to time, and stirring, till a portion of the fused metal, taken out and exposed to the air, no longer assumes an indigo colour, changing to violet or rose and disappearing on cooling, but a fine green or golden tint, which it retains on cooling; then leaving the metal to cool slowly, on a hot sand-bath, for instance, till a crust forms on the surface; piercing this crust with a hot coal; and pouring out the portion which still remains liquid. On subsequently detaching the crust, the inner surface of the metal is found to be covered with beautiful fretted cubes, like those of common salt.

Bismuth is moderately hard, slightly sonorous, and brittle, but may be somewhat extended by careful hammering. Its colour is reddish tin-white, with moderate lustre. The specific gravity of pure bismuth is 9·6542 (Karsten), 9·799 (Marchand and Scherer); of commercial bismuth, 9·822 (Brisson), 9·833 (Herapath), 9·861 (Bergman). Strong pressure rather diminishes than increases the density. Bismuth melts at 480° (Crichton); at 507° (Rudberg); at 509° (Hermann); and expands in solidifying. It boils at an incipient white heat, and if the air be excluded, sublimes in laminæ.

Bismuth forms four compounds with oxygen, viz., the bioxide, BiO_2; the teroxide, BiO_3; the quadroxide BiO_4; and bismuthic acid, BiO_5.

Bioxide or *suboxide of bismuth.*—Bismuth oxidises slowly when exposed to the air at ordinary temperatures, becoming covered with a brownish film of suboxide. When heated in the air till it fuses, it oxidates more rapidly, becoming covered

with the same brown oxide, which is renewed as often as it is removed, till the whole of the metal is oxidised. This sub-oxide is also formed when subnitrate of bismuth is heated with protochloride of tin. By pouring a hydrochloric acid solution of equivalent quantities of teroxide of bismuth and proto-chloride of tin into excess of moderately strong potash, a black-brown precipitate is formed, consisting of a lower oxide of bismuth combined with stannic acid; and on treating this compound with stronger potash, the stannic acid dissolves and an oxide of bismuth remains, which, when dried in vacuo, or at 100°, out of contact with the air, forms a blackish-grey crystalline powder, consisting of BiO_2, retaining, however, a small quantity of water. It shows but little disposition to absorb oxygen at ordinary temperatures, but when heated, it is instantly converted, with a glimmering light, into teroxide. Acids decompose it into metallic bismuth and teroxide. When ignited in an atmosphere of carbonic acid, it becomes perfectly anhydrous, and in that state does not undergo any perceptible alteration by exposure to the air at ordinary temperatures, and oxidises but slowly even at a red heat (R. Schneider).*

Teroxide of Bismuth, BiO_3; 237 or 3662·5. — Bismuth heated in the air till it boils, takes fire and burns with a faint bluish white flame, forming teroxide of bismuth, the vapour of which condenses on the surface of cold bodies in the form of *flowers of bismuth*. The same oxide is obtained in solution by acting on bismuth with nitric acid, the metal being then dissolved with evolution of nitrous fumes. Strong sulphuric acid likewise dissolves it at a boiling heat, with evolution of sulphurous acid. Hydrochloric acid acts but slightly on it, even with the aid of heat. When the solution of the nitrate is mixed with water, a white precipitate of subnitrate is produced; and this, when gently ignited, yields the teroxide in the form of a lemon-yellow powder. By fusing the

* Pogg. Ann. lxxxviii. 45.

hydrated oxide with hydrate of potash, or boiling it with potash-ley, the anhydrous oxide may be obtained in yellow shining needles. Teroxide of bismuth fuses at a strong red heat, and solidifies in a crystalline mass on cooling. It is easily reduced to the metallic state by potassium or sodium at a gentle heat, and by charcoal before the blowpipe.

Teroxide of bismuth combines with acids, forming salts which are very heavy, colourless, unless the acid itself is coloured, and exert a poisonous action. Heated on charcoal with carbonate of soda, they yield a button of metal. *Zinc, tin, cadmium, iron,* and *lead,* precipitate the metal from the solutions of these salts. *Water* decomposes most bismuth-salts —provided they do not contain too large an excess of acid, throwing down a sparingly soluble basic salt, while the acid remains in solution, together with a small quantity of oxide. *Hydrosulphuric acid* produces a brown-black precipitate of tersulphide of bismuth, insoluble in sulphide of ammonium. *Caustic alkalies,* at ordinary temperatures, throw down the white hydrated oxide, but at a boiling heat, especially if they are concentrated, they produce a yellow precipitate of the anhydrous oxide: these precipitates are insoluble in excess of the alkali. *Alkaline carbonates* throw down a white precipitate of carbonate of bismuth, slightly soluble in excess, but precipitated from the solution by a caustic alkali. *Chromate* or *bichromate of potash* throws down a yellow chromate of bismuth, insoluble in caustic potash, whereby it is distinguished from chromate of lead. Sulphuric acid produces no precipitate.

Quadroxide of bismuth, BiO_4.—When a bismuth-salt contains free chlorine, caustic potash produces in it, not a white but a yellow precipitate, which consists of the hydrate of a higher oxide, but cannot be obtained free from chlorine. When this yellow hydrate is boiled with an alkaline chlorite having a strong alkaline reaction, it turns brown, like peroxide of lead, and is converted into the quadroxide of bismuth (Arppe).

This oxide is completely dissolved by boiling nitric acid; any yellow or green residue that may be left, consists of bismuthic acid. It is perhaps a compound of teroxide of bismuth with bismuthic acid: $BiO_3 \cdot BiO_5$.

Bismuthic acid, BiO_5.—Prepared by passing chlorine through a strong solution of potash in which finely divided teroxide of bismuth is suspended; also, by heating a mixture of potash and teroxide of bismuth for a long time in contact with the air,—or better, by calcining a mixture of teroxide of bismuth, caustic potash, and chlorate of potash. Bismuthic acid, prepared by any of these methods, is always more or less mixed with teroxide of bismuth, which, however, may be dissolved out by weak nitric acid. Bismuthic acid is a light red powder, which, at a temperature a little above 212°, gives off part of its oxygen, and is converted into quadroxide of bismuth. Strong acids also decompose it, reducing it to the state of teroxide of bismuth, which then unites with the acid. Bismuthic acid combines with potash, and forms a few double salts, whose bases are the alkali and teroxide of bismuth.

Bisulphide of bismuth, BiS_2, separates in crystals from a fused mixture of metallic bismuth and the tersulphide, and may also be obtained by fusing 10 parts of bismuth with 3 parts of sulphur, melting the resulting mixture three times with fresh sulphur, and cooling quickly. Hydrochloric acid decomposes this compound, yielding metallic bismuth and the terchloride. Hence, and from the fact that its crystalline form is the same as that of the tersulphide, and that by fusing the tersulphide with metallic bismuth, in certain proportions, crystals may be obtained of the same form but containing less sulphur, Schneider concludes that the supposed bisulphide is merely a mixture of the tersulphide with metallic bismuth.

Tersulphide of bismuth, BiS_3, occurs native as *bismuth-glance,* and may be formed artificially by fusing bismuth with

sulphur, and by decomposing bismuth-salts with hydrosulphuric acid. The native variety forms right rhombic prisms, isomorphous with sulphide of antimony: its colour is light lead-grey; specific gravity from 6·4 to 6·5. Tersulphide of bismuth is decomposed by heat; the native sulphide, heated in a tube, yields sublimed sulphur; and the artificial sulphide, when fused and left to cool, yields globules of metallic bismuth as it solidifies.

Selenide of bismuth, $BiSe_3$, is obtained by melting together 1 eq. of bismuth and 3 eq. of selenium, and remelting the product with fresh selenium out of contact with the air. On a recently fractured surface, it exhibits a steel-grey colour, metallic lustre, and a distinct crystalline laminated texture. Its density is 6·82; hardness equal to that of galena: it may be readily pulverised. It is scarcely attacked by hydrochloric acid, but nitric acid and aqua regia decompose it readily (Schneider).

Bichloride of bismuth, $BiCl_2$, is formed by the action of dry hydrogen on the terchloride of bismuth and ammonium, $2NH_4Cl.BiCl_3$, at about 570°, or by heating 1 part of pulverised bismuth with 2 parts of subchloride of mercury in a sealed tube, at about 460°, and purifying the product by repeated fusion in sealed tubes. It is a black hygroscopic mass, which, by heating in the air, and by the action of acids, is resolved into metallic bismuth and the terchloride.

Terchloride of bismuth, $BiCl_3$.—Pulverised bismuth thrown into chlorine gas takes fire and burns with a pale blue light, forming the terchloride. This compound may also be obtained by heating 1 part of bismuth with 2 parts of protochloride of mercury, or by evaporating to dryness the solution of teroxide of bismuth in hydrochloric acid, and distilling the residue out of contact with the air. It is a white opaque solid, with a slight tinge of brown or grey, and a granular fracture; melts very readily, forming an oily liquid. The *hydrated*

terchloride is obtained in crystals by dissolving the teroxide in hydrochloric acid, and evaporating. The anhydrous chloride, the crystals, and the solution are decomposed by water, yielding *oxychloride of bismuth*, $BiCl_3 . 2BiO_3$, in the form of an insoluble white powder, commonly known as *pearl-white*,—and hydrochloric acid holding a small quantity of bismuth in solution. A *sulphochloride*, of analogous composition, $BiCl_3 . 2BiS_3$, is obtained by heating chloride of bismuth and ammonium with sulphur or tersulphide of bismuth, or by passing hydrosulphuric acid gas over the same compound, heated to a temperature between 485° and 572°, and afterwards heating the product to its melting point in the same gas :—

$$3BiCl_3 + 6HS = BiCl_3 . 2BiS_3 + 6HCl.$$

The product of either of these operations, after being washed, first with water containing so much hydrochloric acid as not to give a precipitate with the terchloride, then with water slightly acidulated, and lastly with pure water, forms small, dark grey, crystalline needles, which, when heated in the air, give off, first, chloride of bismuth, then sulphurous acid, and leave a mixture of oxychloride and basic sulphate of bismuth (Schneider). A *seleniochloride*, $BiCl_3 . 2BiSe_3$, is obtained by adding terselenide of bismuth to fused chloride of bismuth and ammonium. It forms small needle-shaped crystals, having a dark steel-grey colour and metallic lustre (Schneider).

Terchloride of bismuth and ammonium.— A solution of 1 eq. of terchloride of bismuth and 2 eq. of sal-ammoniac, yields, by evaporation, double six-sided pyramids containing $2NH_4Cl . BiCl_3$, isomorphous with the corresponding terchloride of antimony and ammonium (Jacquelain). A solution of 1 eq. terchloride of bismuth and 6 eq. sal-ammoniac yields rhombic crystals, containing $3NH_4Cl . BiCl_3$ (Arppe).

Bismuth dissolves in a boiling solution of protochloride of copper, the liquid being decolorised, and appearing to contain the compound, $3Cu_2Cl . BiCl_3$. Bismuth dissolves in a similar manner in other cupric salts (Schneider).

Teriodide of bismuth, BiI_3.— Obtained as a crystalline sublimate by heating 1 eq. (32 parts) of tersulphide of bismuth with 3 eq. (475 parts) of iodine. Large, thin, crystalline laminæ, having the form of regular six-sided prisms, of a blackish grey colour with a tinge of brown and a strong lustre. The compound, heated in the air, volatilises for the most part, leaving a small quantity of basic oxide of bismuth of a red-brown colour. Boiling water converts it into the same compound. Aqueous potash decomposes it, forming iodate of bismuth, $BiO_3 . 3IO_3$: the same change is more slowly produced by alkaline carbonates. Alkaline sulphides decompose it, forming tersulphide of bismuth. Hydrochloric acid dissolves it without decomposition; nitric acid, with separation of iodine.

Sulphates of bismuth.—When bismuth is heated with strong sulphuric acid, sulphurous acid is evolved, and the metal is converted into a white insoluble powder, consisting of *tersulphate of bismuth*, $BiO_3 . 3SO_3$, which is decomposed by water, yielding a very acid salt which dissolves, and a *monobasic sulphate*, $BiO_3 . SO_3 + HO$, which remains. There is also a *bisulphate of bismuth*, which is obtained in small delicate needles when an acid solution of nitrate of bismuth is mixed with sulphuric acid (Heintz).

Carbonate of bismuth, $BiO_3 . CO_2$, is obtained by adding nitrate of bismuth to the solution of an alkaline carbonate: this salt is used in medicine.

Nitrates of bismuth. — The *neutral* or *ternitrate*, $BiO_3 . 3NO_5 + 10HO$, is obtained by dissolving bismuth in hot nitric acid, evaporating the solution, and leaving it to cool. The salt then separates in transparent oblique prisms of six or eight sides, and terminated with several faces. At 212°

they separate into a solid and a liquid portion, the latter solidifying as it cools. At 302°, they are reduced to the mononitrate, $BiO_3 . NO_5 + HO$; which, when further heated to 500°, gives up all its acid and water, and leaves oxide of bismuth.

Subnitrates of bismuth.—a. Ternitrate of bismuth dissolves without decomposition in a small quantity of water, especially if a few drops of nitric acid are added. But a larger quantity of water decomposes it, forming a white precipitate of a subsalt, commonly called *magistery of bismuth.* This substance is generally regarded as a mononitrate containing one atom of water, $BiO_3 . NO_5 + HO$; but, according to Becker *, the basic nitrate obtained directly by treating the ternitrate with cold water, consists of $BiO_3 . NO_5 + 2 HO$. This precipitate, when recently formed, dissolves somewhat freely in water, especially if the water contains nitric acid. Hence, if, after the precipitation of the basic salt, the supernatant liquid be mixed with a large quantity of water, the precipitate is completely redissolved; but after a while, a basic salt separates, containing $5BiO_3 . 4NO_5 + 9Aq$; this, according to Becker, is the true magistery of bismuth, inasmuch as, in the usual mode of preparing that substance, the same change takes place in washing the precipitate. Boiling water decomposes this salt, extracting all the nitric acid, excepting about 1 per cent.—*b.* A salt containing $5BiO_3 . 4NO_5 + 12HO$, is obtained by evaporating a solution of the ternitrate at a strong heat. When the precipitate first obtained by the action of cold water on a solution of the ternitrate is heated in contact with a free acid, or when the same acid solution is poured into hot water, a white, very loose powder is precipitated, containing $6BiO_3 . 5NO_5 + 9HO$. This salt is decomposed by water more readily than the preceding. If it be washed with water as long as the filtrate continues to

* Archiv. Pharm. lv. 31. and 129.

exhibit a strong acid reaction, a crystalline residue is left on the filter, containing $4BiO_3 . 3NO_5 . 9Aq$. Duflos obtained a *magistery of bismuth* having the same composition, by treating the crystals of the neutral nitrate with 24 times their weight of water. Lastly, if the mononitrate, completely freed from the adhering acid liquid, be treated with water likewise free from acid, it dissolves completely; but the liquid after a while becomes milky, and after long standing deposits a white amorphous powder, containing $5BiO_3 . 3NO_5 + 8HO$. This salt may be formed, in addition to the true magistery of bismuth, if, in the preparation of that substance, too large a quantity of water be used, and the greater part of the acid liquid removed (Becker.) Magistery of bismuth is used as a cosmetic, but has the serious disadvantage of being blackened by hydrosulphuric acid.

Bichromate of bismuth, $BiO_3 . 2CrO_3$.—When a solution of ternitrate of bismuth, containing as little free acid as possible, is poured into a moderately concentrated solution of bichromate of potash, bichromate of bismuth is obtained in the form of a yellow flocculent precipitate, which becomes dense and crystalline after a while, or immediately if heated. It may be dried without decomposition between 212° and 257°, but becomes blackish-green at a red heat. It contains 69·48 per cent. of teroxide of bismuth (J. Löwe.)

The *alloys* of bismuth are remarkable for their fusibility. The amalgam of this metal is liquid. An alloy of 8 parts bismuth, 5 lead, and 3 tin, melts at 202°; another mixture of 2 bismuth, 1 lead, and 1 tin, at 200·75°: these mixtures are known by the name of *fusible metal*. Bismuth is also added to the alloy of tin and lead used for casting stereotype plates. Besides increased fusibility, bismuth communicates to this alloy the property of expanding on becoming solid, by which it is rendered capable of taking an accurate impression.

ESTIMATION OF BISMUTH, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

The best reagent for precipitating bismuth from its solutions is carbonate of ammonia; which, when added in excess, throws down the bismuth completely: the liquid must, however, be left to stand for some hours in a warm place, otherwise a considerable quantity of the bismuth will remain in solution. The precipitate, after being washed and dried, must be separated from the filter as completely as possible, the filter separately burned, and the precipitate ignited in a porcelain crucible: a platinum crucible would be attacked by it: after ignition, it consists of teroxide of bismuth containing 89·66 per cent. of the metal.

If the solution contains hydrochloric acid, the bismuth cannot be estimated by precipitation with carbonate of ammonia, or any other alkali, because the precipitate so produced would contain oxychloride of bismuth (p. 255). In this case, therefore, the bismuth must be precipitated by hydrosulphuric acid; the sulphide of bismuth oxidised and dissolved by nitric acid; and the diluted solution treated with carbonate of ammonia, as above.

Bismuth is separated from the *alkalies* and *earths*, and from *iron, cobalt, nickel, zinc,* and *chromium*, by hydrosulphuric acid; from *tin, arsenic,* and *antimony*, by sulphide of ammonium; from *lead*, by sulphuric acid; and from *copper* and *cadmium* by ammonia. The separation of bismuth from cadmium may also be effected by cyanide of potassium, which dissolves the latter as cyanide of cadmium and potassium, and precipitates the bismuth. The precipitated bismuth, however, always contains potash, and must therefore be dissolved in nitric acid and precipitated by carbonate of ammonia. These two metals may also be separated by means of bichromate of potash, which throws down the bismuth as $BiO_3 . 2\ CrO_3$, and retains the cadmium in solution.

ORDER VII.

METALS NOT INCLUDED IN THE FOREGOING CLASSES, WHOSE OXIDES ARE NOT REDUCED BY HEAT ALONE.

SECTION I.

URANIUM.

Eq. 60, *or* 750; U.

THIS metal is obtained from *pitchblende,* a mineral containing from 40 to 95 per cent. of uranoso-uranic oxide, U_3O_4, associated with sulphur, arsenic, lead, iron, and several other metals. The mineral is finely pounded; freed by elutriation from the finer earthy impurities; roasted for a short time, to remove part of the sulphur and arsenic; then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water; the solution filtered from the brick-red residue of ferric oxide, ferric arseniate, and lead-sulphate; the greenish yellow filtrate slightly concentrated by evaporation, and left to cool, whereupon it deposits crystals; and the resulting radiated mass of crystallised uranic nitrate drained on a funnel, and then washed with a small quantity of cold water. As the water dissolves a portion of the crystals, it is used in a subsequent operation to redissolve the residue obtained by evaporating the solution of pitchblende in nitric acid. The uranic nitrate, after being dried in the air, is introduced into a wide-mouthed bottle containing ether, in which it immediately dissolves; the yellow solution is left to evaporate in the air; and the resulting crystals are purified

by solution in hot water and recrystallisation. The mixed mother-liquids, after dilution with water, are treated with hydrosulphuric acid to precipitate arsenic, lead, and copper, and the filtrate is freed from oxide of iron by evaporating to dryness and digesting the residue in water. The solution thus obtained yields a fresh crop of crystals of uranic nitrate. This salt is converted by ignition into uranoso-uranic oxide, U_3O_4, and from this the protoxide is obtained by ignition with reducing agents (Péligot).

Metallic uranium is obtained by decomposing the protochloride with potassium or sodium. If the mixture be heated in a platinum crucible over a spirit-lamp, and the soluble alkaline chloride washed out by water, the uranium is obtained in the form of a black powder, or sometimes aggregated on the sides of the crucible in small plates, having a silvery lustre and a certain degree of malleability. But, by introducing into a porcelain crucible, first, a layer of sodium, then chloride of potassium, and then a mixture of chloride of potassium and protochloride of uranium (the use of the chloride of potassium being to moderate the action, which is otherwise very violent), placing the porcelain crucible within a closed earthen crucible lined with charcoal, and heating it, first moderately, till the reduction takes place, and then strongly in a blast-furnace for 15 or 20 minutes, the metal is obtained in fused globules (Péligot).

Uranium, in its compact state, is somewhat malleable and hard, but is scratched by steel. Its specific gravity is 18·4; its colour is like that of nickel or iron. When exposed to the air, it soon tarnishes and assumes a yellowish colour. At a red heat it oxidises with vivid incandescence, and becomes covered with a bulky layer of black oxide, which protects the interior from oxidation. In the pulverulent state, it takes fire at about 402°, burning with great splendour, and forming a dark-green oxide. It is permanent in the air at ordinary temperatures, and does not decompose cold water.

It dissolves with evolution of hydrogen in dilute acids, forming green solutions. It combines directly with chlorine, giving out great light and heat, and forming a green volatile chloride. It unites directly with sulphur at a slightly elevated temperature (Péligot).

Uranium forms four compounds with oxygen, viz., the *protoxide*, UO; the *sesquioxide*, U_2O_3; and two intermediate oxides, U_4O_5, and, U_3O_4, which may be regarded as compounds of the other two, viz., $2UO.U_2O_3$ and $UO.U_2O_3$.

Protoxide of uranium; Uranous oxide, UO, 68, or 850.—This oxide is obtained by exposing uranoso-uranic oxide, mixed with charcoal powder, bullock's blood, or oil, to the strongest heat of a blast-furnace; by heating the same oxide to redness in a current of dry hydrogen; by igniting uranic oxalate out of contact of air, or better, in a current of hydrogen; or by igniting the chloride of uranyl and potassium (p. 257), either alone or in a current of hydrogen. Protoxide of uranium has sometimes the form of an earthy powder of a grey or brown colour; sometimes of crystalline scales having the metallic lustre. It was for a long time regarded as metallic uranium,* till Péligot† pointed out its true nature, and obtained the real metal in the manner above mentioned.

Uranous oxide, after ignition, is insoluble in boiling dilute hydrochloric or sulphuric acid, but dissolves in strong sulphuric acid. The hydrated oxide dissolves readily in acids. Solutions of uranous salts are green, and, when treated with alkalies or alkaline carbonates, or with carbonate of lime, yield a reddish-brown gelatinous hydrate of uranous oxide, which dissolves in alkaline carbonates, especially in carbonate of ammonia, forming a green solution. Alkaline hydrosulphates yield a black precipitate of uranous sulphide. Uranous salts are converted into uranic salts by exposure to the air, by

* See the first edition of this work, page 643.

† Ann. Ch. Phys. [3.], v. 5.; and xii. 258.

the action of nitric acid, and by gold and silver salts; the action in the last case being accompanied by precipitation of metallic gold or silver.

Protochloride of uranium; Uranous chloride, UCl, is obtained by burning uranium in chlorine gas, or by passing that gas over an intimate mixture of charcoal and either of the oxides of uranium, strongly heated in a tube of very refractory glass. It crystallises in dark-green regular octohedrons, which have a metallic lustre, and, when heated to redness, volatilise in red vapours and form a sublimate. It fumes strongly on exposure to the air, and dissolves very readily in water, forming a green solution.

Uranous sulphate, $UO.SO_3$, is found native as *uranium-vitriol*, and may be formed artificially by dissolving uranoso-uranic oxide in boiling oil of vitriol; or hydrated uranous oxide in dilute sulphuric acid; or by decomposing a concentrated solution of uranous chloride with sulphuric acid. Crystallises with two and with four atoms of water. A *bibasic uranous sulphate* is obtained by treating the normal salt with a large quantity of water; by exposing the alcoholic solution of that salt to the sun's rays; by careful addition of ammonia to its aqueous solution; and by boiling that solution with green uranoso-uranic oxide. It forms a light-green powder having a silky lustre.

Uranoso-uranic oxide, U_3O_4, or $UO.U_2O_3$.—This oxide forms the principal constituent of pitchblende. It is obtained artificially by burning the metal or the protoxide in the air; by heating the protoxide to redness in an atmosphere of aqueous vapour; and by gentle ignition of uranic oxide or uranic nitrate. It is a dark-green powder which dissolves in acids, forming green solutions, exhibiting characters intermediate between those of uranous and uranic salts, and probably consisting of mere mixtures of the two.

Another intermediate oxide, U_4O_5, or $2UO.U_2O_3$, is said to be formed by strongly igniting the last oxide or the sesqui-

oxide. It is black, and dissolves in acids, like the last; but it is probably a mere mixture of U_3O_4 with the protoxide.

Sesquioxide of uranium; Uranic oxide, U_2O_3; 144, *or* 1800.—Uranium and its lower oxides dissolve in nitric acid, with evolution of nitric oxide and formation of uranic nitrate. When a solution of this salt in absolute alcohol is evaporated at a gentle heat, till nitrous ether begins to escape, an orange-yellow spongy mass is obtained, consisting of hydrated uranic oxide mixed with undecomposed nitrate: the nitrate may be dissolved out by water, and the hydrated oxide then remains, exhibiting a lemon-yellow or orange-yellow colour. This hydrate is permanent in the air, and does not absorb carbonic acid. At 572°, it yields anhydrous uranic oxide, which is also yellow; and at a low red heat, it is converted into green uranoso-uranic oxide.

The *uranic* salts are obtained by oxidising uranous or uranoso-uranic salts with nitric acid, or by exposing them to the air. Most of them contain one equivalent of uranic oxide combined with one equivalent of an acid. Now, as this is contrary to the usual analogy of the normal salts of sesquioxides, most of which contain three equivalents of acid to one equivalent of base, *e.g.*, ferric sulphate $= Fe_2O_3 . 3SO_3$; sulphate of alumina $= Al_2O_3 . 3SO_3$,—Péligot is of opinion that the base of these salts is not really a sesquioxide, but the protoxide of a compound radical *uranyl,* U_2O_2, made up of the elements of 2 equivalents of uranous oxide: $U_2O_3 = (U_2O_2)\,O$. To abbreviate the formulæ, we shall denote the compound radical, uranyl, by the symbol U'; we have then for the formula of uranic sulphate: $U_2O_3 . SO_3 = (U_2O_2)\,O . SO_3 = U'O . SO_3$.

Uranic salts are yellow; they are mostly soluble in water, and, in solution, have a very rough taste, without any metallic after-taste. They are reduced to uranous salts by *hydrosulphuric acid;* also by *alcohol* or *ether,* in sunshine. *Caustic alkalies* added to uranic solutions throw down a yellow precipitate, consisting of a uranate of the alkali, which is insoluble

in excess of the reagent. *Alkaline carbonates* produce a yellow precipitate, consisting of a carbonate of uranic oxide and the alkali, soluble in excess, especially in bicarbonate of potash or sesquicarbonate of ammonia. Potash added to these solutions throws down all the uranic oxide. From the solution in carbonate of ammonia, the uranic oxide is likewise precipitated by boiling. *Carbonate of baryta* precipitates uranic oxide completely from its solutions at ordinary temperatures. *Phosphate of soda,* added to uranic salts not containing too much free acid, produces a white precipitate of uranic phosphate, having a slight tinge of yellow. *Sulphide of ammonium* produces a black precipitate of uranic sulphide, which remains for a long time suspended in the liquid. *Hydrosulphuric acid* produces no precipitate. *Ferrocyanide of potassium* produces a dark red-brown precipitate; *ferricyanide of potassium,* none. Metallic *zinc* does not precipitate uranium in the metallic state from uranic solutions, but, after a long time, produces a yellow precipitate of uranic oxide.

Uranic oxide and its salts, fused with *phosphorus-salt* in the outer blowpipe flame, produce a clear yellow glass which becomes greenish on cooling. In the inner flame, the glass assumes a green colour, becoming still greener when cold. Similar colours with *borax.* The oxides of uranium are not reduced to the metallic state by fusion with carbonate of soda on charcoal. Uranic oxide is used for imparting a delicate yellow tint to glass; the glass thus coloured is called *canary glass.*

Chloride of uranyl, $U_2O_2Cl = U'Cl$.—When dry chlorine gas is passed over uranous oxide at a red heat, the tube becomes filled with an orange-yellow vapour of this compound, which solidifies in a yellow crystalline mass, easily fusible, but not very volatile. Dissolved in water, it forms hydrated chloride of uranyl, or hydrochlorate of uranic oxide:

$$U_2O_2Cl + HO = U_2O_3 . HCl.$$

Chloride of uranyl and potassium, $KCl \, . \, U \, Cl + 2Aq.$, is formed by evaporating an aqueous mixture of uranic chloride and chloride of potassium. By heating the hydrated crystals to 212°, the anhydrous compound is obtained.

Uranic sulphate; sulphate of uranyl.—The monosulphate $V'O \, . \, SO_3 + 3Aq.$ is obtained by dissolving uranoso-uranic oxide in strong sulphuric acid, diluting the solution with water, and oxidising with nitric acid; also by decomposing a solution of uranic nitrate with sulphuric acid, expelling the excess of acid by heat, dissolving the residue in water, evaporating the solution to a syrup, and leaving it to crystallise. Forms small lemon-yellow prisms. According to Berzelius, a *bisulphate* and a *tersulphate* are obtained by dissolving the monosulphate in sulphuric acid; but Péligot denies their existence. A basic sulphate is found native in the form of a yellow powder. The monosulphate forms, with sulphate of potash, a crystalline double salt, whose formula is:

$$KO.SO_3 + U_2O_3 \, . \, SO_3 + 2HO = \left.\begin{matrix} K \\ U' \end{matrix}\right\} 2SO_4 + 2HO.$$

Uranic nitrate; nitrate of uranyl; $U_2O_3.NO_5 = U'O.NO_5$, is formed by treating the metal or either of its oxides with nitric acid. It crystallises in lemon-yellow prisms. The solution of this salt possesses the power of lowering the refrangibility of rays of light which fall upon it, producing the peculiar phenomenon called *fluorescence*. This property is likewise exhibited by other compounds of uranium, especially by *canary-glass*. A *basic* nitrate is formed by gently igniting the normal salt.

Uranic phosphates; phosphates of uranyl.—Three of these salts are known, all containing 3 atoms of base to 1 atom of acid. When uranic oxide is digested in a small quantity of aqueous phosphoric acid, a yellow saline mass is produced, part of which dissolves in boiling water, leaving a light yellow powder, which is the *neutral phosphate* $(2U'O \, . \, HO) \, . \, PO_5$. The aqueous solution concentrated by heat, and then left

to evaporate in vacuo over oil of vitriol, deposits a lemon-yellow crystalline salt, consisting of the *acid phosphate* $(U'O . 2HO) . PO_5$. The *basic phosphate* has not been obtained in the separate state; but when uranic nitrate is mixed with a moderate excess of basic phosphate of soda $(3NaO . PO_5)$, a dark yellow precipitate is formed containing $(NaO . 2U'O) . PO_5 + 3U'O . PO_5$ (Wertheim).* When uranic acetate is added to a solution of any soluble phosphate containing an abundance of ammonia and free acetic acid, a yellow precipitate is formed consisting of *ammonio-uranic phosphate*, $2U'O . NH_4O . PO_5$, which, when ignited, leaves uranic pyrophosphate, $2U'O . PO_5$. This reaction affords a ready and exact method of estimating phosphoric acid. The insoluble phosphates, even those of alumina and sesquioxide of iron, are also decomposed by boiling with uranic acetate in presence of a large excess of acetate of ammonia and free acetic acid, the bases dissolving, while the phosphoric remains undissolved in the form of the ammonio-uranic phosphate above described. To separate phosphoric acid from iron in this manner requires, however, a very large excess of the uranium-salt (W. Knop).†

A neutral and an acid *arseniate of uranyl*, analogous in composition to the phosphates, have also been obtained by similar means. The composition of these phosphates and arseniates affords a strong argument in favour of the uranyl theory.

Compounds of uranic oxide with bases. — Uranic oxide combines as an acid with the alkalies, earths, and other metallic oxides, forming salts which may be called *uranates*. The uranates of the alkalies are obtained by precipitating a solution of uranic oxide in an acid with an alkali; the uranates of the earths and heavy metallic oxides, by adding ammonia to a solution of an uranic salt mixed with one of

* J. pr. Chem. xliii. 321.

† Chem. Gaz. 1856, 467.

these bases. The uranates are for the most part yellow, and after ignition orange-yellow. The soda-compound, $NaO . 2U_2O_3 + 6HO$, is used for colouring glass, and is prepared on the large scale by roasting pitchblende with limestone in a reverberatory furnace; treating the resulting uranate of lime with dilute sulphuric acid, by which the uranic oxide is almost completely dissolved; mixing the green solution with crude carbonate of soda, by which the uranium is precipitated together with other metals, but redissolved tolerably free from impurities by excess of the alkali; and treating the liquid with dilute sulphuric acid as long as effervescence is produced. The uranate of soda is then precipitated in a form well adapted for the manufacture of yellow glass.

ESTIMATION OF URANIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Uranium is completely precipitated from uranic solutions by ammonia. The precipitate, which consists of hydrated uranic oxide containing ammonia, must be washed with water containing sal-ammoniac, as it runs through the filter when washed with pure water. It is then dried and ignited in an open crucible, whereby it is converted into uranoso-uranic oxide, U_3O_4; but to obtain a perfectly definite result, and prevent further oxidation during cooling, it is necessary to put the cover on the crucible while the substance is still red-hot, and keep it there till the crucible is quite cold. The oxide thus obtained contains 84·90 per cent. of uranium. An accurate result is likewise obtained by igniting the sesquioxide in an atmosphere of hydrogen, whereby it is reduced to protoxide containing 88·24 per cent. of the metal.

If the uranic solution contains a considerable quantity of an earth or a fixed alkali, the precipitate formed by ammonia carries down with it a certain portion of the earth or alkali;

to free it from which it must, before ignition, be redissolved in hydrochloric acid and reprecipitated by ammonia.

From the *fixed alkalies,* uranium, in the state of sesquioxide, is separated by ammonia, attention being paid to the precaution just mentioned.

From *baryta* it is separated by sulphuric acid; from *strontia* and *lime,* also by sulphuric acid with addition of alcohol.

From *magnesia, manganese, cobalt, nickel, and zinc,* these metals being in the state of protoxide, and the uranium in the state of sesquioxide, it is separated by precipitation with carbonate of baryta.

From *iron* it is separated by carbonate of ammonia, both metals being in the state of sesquioxide; the uranic oxide then dissolves, while the ferric oxide remains undissolved. Care must, however, be taken that the carbonate of ammonia be really monocarbonate, quite free from excess of carbonic acid, otherwise the iron will also be dissolved. To ensure this condition, the carbonate of ammonia must be previously boiled, and the solution of the oxides, if acid, must be neutralised with ammonia till a slight permanent precipitate begins to form: the solution should then be diluted with water. The uranic oxide is separated from the filtrate either by boiling, or by supersaturation with hydrochloric acid and precipitation by ammonia.

From *alumina,* uranium is also separated by carbonate of ammonia, and with greater facility.

From *cadmium, copper, lead, tin, arsenic, antimony,* and *bismuth,* uranium is separated by hydrosulphuric acid; from *titanium* and *chromium* in the same manner as iron is separated from those metals (pp. 152. 171.); and from *vanadium, tungsten, molybdenum,* and *tellurium,* by sulphide of ammonium, in which the sulphides of the last named metals are soluble.

SECTION II.

CERIUM.

Eq. 47·26, *or* 590·87. Ce.

This metal, which was discovered in 1803, simultaneously by Klaproth, and by Hisinger and Berzelius, exists, together with lanthanum and didymium, in cerite, allanite, orthite, yttro-cerite, and a few other minerals, all of somewhat rare occurrence. The most abundant of them is cerite, which is a compound of silicic acid with the oxides of cerium, lanthanum, and didymium, together with small quantities of lime and oxide of iron. To extract the oxides of the three metals, the cerite is finely pounded and boiled for some hours with strong hydrochloric acid, or aqua-regia, which dissolves the metallic oxides, leaving nothing but silica. The filtered solution is then treated with a slight excess of ammonia, which precipitates everything but the lime; the precipitate is redissolved in hydrochloric acid, and the solution treated with excess of oxalic acid. A white or faintly rose-coloured precipitate is then obtained, consisting of the oxalates of cerium, lanthanum, and didymium: it is curdy at first, but in a few minutes becomes crystalline, and easily settles down. When dried and ignited, it yields a red-brown powder, containing the three metals in the state of oxide. The finely pounded cerite may also be mixed with strong sulphuric acid to the consistence of a thick paste, the mixture gently heated till it is converted into a dry white powder, and this powder heated somewhat below redness in an earthen crucible. The three metals are thus brought to the state of basic sulphates, which dissolve completely when very gradually added to cold water; and the solution treated with oxalic acid yields a precipitate of the mixed oxalates, which may be ignited as before.

From the red-brown mixture of the oxides of cerium, lanthanum, and didymium thus obtained, a pure oxide of cerium

may be prepared by either of the following processes :—1. The mixed oxides are heated with strong hydrochloric acid, which dissolves the whole, with evolution of chlorine; the solution precipitated with excess of caustic potash; and chlorine gas passed through the liquid with the precipitate suspended in it. The cerium is thereby brought to the state of sesqui-oxide, which is left undissolved in the form of a bright yellow precipitate, while the lanthanum and didymium remain in the state of protoxides, and dissolve. To ensure complete separation, the passage of the chlorine must be continued till the liquid is completely saturated with it, and the solution, together with the precipitate, left for several hours in a stoppered bottle, and agitated now and then. The liquid is then filtered, the washed precipitate treated with strong boiling hydrochloric acid, which dissolves it with evolution of chlorine, and forms a colourless solution of proto-chloride of cerium; and this, when treated with oxalic acid or oxalate of ammonia, yields a perfectly white precipitate of oxalate of cerium, which may be converted into oxide by ignition (Mosander). 2. The red-brown mixture of the three oxides is treated with very dilute nitric acid (1 part of nitric acid of ordinary strength to between 50 and 100 parts of water), which dissolves the greater part of the oxides of lanthanum and didymium, and leaves the oxide of cerium; and by treating the residue with very strong nitric acid, the last traces of lanthanum and didymium may be extracted (Mosander, Marignac). 3. The red-brown mixture of the three oxides is boiled for several hours in a strong solution of chloride of ammonium. The oxides of lanthanum and didymium then dissolve, with evolution of ammonia, and ceric or ceroso-ceric oxide is left in a state of purity. It must be collected on a filter and washed with a solution of sal-ammoniac, because, when washed with pure water, it first runs through the filter, and then stops it up (Watts).*

* Chem. Soc. Qu. J. ii. 147.

Metallic cerium is obtained by heating the pure anhydrous protochloride with potassium or sodium. It is a grey powder which acquires the metallic lustre by pressure. It oxidises readily, decomposes water slowly at ordinary temperatures, quickly at the boiling heat, and dissolves rapidly in dilute acids, with evolution of hydrogen, forming a solution of a cerous salt.

Protoxide of cerium; Cerous oxide, CeO; 55·26 or 690·8.—This oxide is scarcely known in the anhydrous state. The sesquioxide, exposed to the strongest heat of a wind-furnace, in a crucible lined with charcoal, yields a residue chiefly consisting of protoxide, but the reduction is never complete. The hydrated protoxide is easily obtained by precipitating the chloride with a caustic alkali. It dissolves readily in acids, forming the *protosalts of cerium* or *cerous salts,* the solutions of which are distinguished by the following characters: *Caustic potash* or *soda* produces a white precipitate of the hydrated protoxide, which is insoluble in excess, and is converted into the yellow sesquioxide by the action of chlorine or hypochlorous acid. *Ammonia* precipitates a basic salt. *Alkaline carbonates* form a white precipitate of cerous carbonate insoluble in excess. *Oxalic acid* or *oxalate of ammonia* produces a white precipitate of cerous oxalate, gelatinous at first, but quickly assuming the crystalline character, and converted by ignition in an open vessel into a salmon-coloured powder, consisting of sesquioxide of cerium mixed with protoxide. Hydrosulphuric acid produces no precipitate. *Sulphide of ammonium* throws down the hydrated protoxide. *Ferrocyanide of potassium* produces a white pulverulent precipitate; ferricyanide of potassium, none. *Sulphate of potash* produces a white crystalline precipitate of potassio-cerous sulphate, nearly insoluble in pure water, and quite insoluble in excess of sulphate of potash. With dilute solutions the precipitate takes some time to form. This character, together with the behaviour of the oxalate, and the

yellow coloration of the hydrated protoxide by chlorine, serves to distinguish cerium from all other metals. Cerous salts in solution have a sweet astringent taste, and redden litmus, even when the acid is perfectly saturated. All compounds of cerium, ignited with *borax* or *phosphorus-salt* in the outer blowpipe-flame, yield a glass which is deep red while hot, but becomes colourless on cooling. In the inner flame a colourless bead is formed, but when ignited with excess of oxide of cerium, it forms a yellow enamel.

Sesquioxide of cerium; Ceric oxide, Ce_2O_3.—It is doubtful whether this oxide has been obtained in the separate state. The hydrated protoxide, the nitrate, and the oxalate, yield, when ignited in the acid, a salmon-coloured powder, which is generally regarded as ceric oxide; but, according to Marignac, it is a mixture or compound of the sesquioxide and protoxide of cerium, not quite constant in composition, but containing on the average 82·15 per cent of metal, and therefore nearly agreeing with the formula Ce_7O_9 or $3CeO.2Ce_2O_3$. When mixed with oxide of didymium, its colour is red-brown. This oxide is nearly insoluble in strong nitric and hydrochloric acids, even at the boiling heat, but strong boiling sulphuric acid dissolves it. Hydrochloric acid, with the aid of reducing agents, such as alcohol, dissolves it slowly at the boiling heat, forming a solution of cerous chloride. If mixed with the oxide of lanthanum or didymium, it dissolves readily in strong boiling hydrochloric acid, with evolution of chlorine. The solution of this oxide in strong sulphuric acid has a bright yellow colour, and deposits yellow prismatic crystals, which, according to Marignac, consist of a *ceroso-ceric-sulphate*, containing $Ce_7O_9 . 4SO_3 + 7HO$. Potash, added to the solution of this salt, throws down a yellow hydrate, which dissolves readily in acids. The solutions are yellow, and, when boiled with hydrochloric acid, are converted into cerous salts.

Protosulphide of cerium, CeS, is obtained by igniting the

carbonate in vapour of bisulphide of carbon, or by heating an oxide of cerium with sulphide of potassium. The first process yields a light powder of the colour of red lead; the second, a product resembling mosaic gold. The *sesquisulphide of cerium* is not known in the free state, but exists in certain sulphur-salts.

Protochloride of cerium, CeCl.—Cerium burns vividly when heated in chlorine gas, and forms this compound. The anhydrous chloride may be prepared by igniting the sulphide, or the residue obtained by evaporating to dryness a solution of the chloride mixed with sal-ammoniac, in a current of chlorine gas. If the air is not completely excluded, an oxychloride is also produced. The anhydrous chloride is a white porous mass, fusible at a red heat, and perfectly soluble in water. A *hydrated chloride* is obtained in colourless four-sided prisms, by dissolving the hydrated oxide or the carbonate in hydrochloric acid, and evaporating to a syrup. The solution, when exposed to the air, turns yellow, from formation of a ceric salt.

Sesquichloride of cerium.—The hydrated sesquioxide dissolves in cold hydrochloric acid, forming a red solution, which, however, soon gives off chlorine, and is reduced, more or less completely, to protochloride.

Protofluoride of cerium is formed by precipitating the protochloride with an alkaline fluoride. The *sesquifluoride* occurs native in six-sided prisms, mixed with half its weight of protofluoride; also with the fluorides of yttrium and calcium, in *yttrocerite.* An oxyfluoride of cerium, $Ce_4F_3O_3+3HO$, is also found native.

Cerous carbonate, $CeO \cdot CO_2+3HO$, is formed by exposing the hydrated protoxide to the air, or by precipitation.

Cerous oxalate, $C_4Ce_2O_8$, is precipitated from cerous salts by oxalic acid or oxalate of ammonia added in excess, even when the solution contains a considerable quantity of free nitric or hydrochloric acid. It is at first curdy, but soon becomes

very dense and crystalline. When ignited with free access of air, it yields ceroso-ceric oxide.

Cerous sulphate, $CeO . SO_3$.—The anhydrous salt is a white powder, which, when sprinkled with a small quantity of water, becomes very hot, and condenses into a solid mass, very difficult to dissolve. It forms two crystalline hydrates, viz., $2(CeO . SO_3) + 3HO$ and $(CeO . SO_3) + 3HO$. The anhydrous salt, heated in a close vessel, leaves a basic cerous sulphate; but, with free contact of air, it leaves a basic ceric or ceroso-ceric sulphate. Cerous sulphate forms with sulphate of potash a crystalline double salt, containing $CeO . SO_3 + KO . SO_3$, which is nearly insoluble in water.

Cerous phosphate.—Obtained by precipitating a cerous salt with phosphate of soda. It also occurs native (associated with the phosphates of lanthanum and didymium), in several forms. In *Monazite* and *Edwardsite*, it occurs in oblique rhombic prisms; in the former it is associated with thorina, and small quantities of lime, manganese, and tin; in the latter, with alumina, zirconia, and silica. *Cryptolite* is a tribasic phosphate of cerium, occurring in the rose-coloured apatite of Arendal in Norway, and is separated by dissolving the apatite in nitric acid. It then remains in the form of a crystalline powder, appearing under the microscope to consist of hexagonal prisms. Sp. gr. 4·6 (Wöhler).* *Phosphocerite* is a mineral similar in composition to cryptolite. It was discovered by Mr. O. Sims in the cobalt-ore of Johannisberg in Sweden, of which it forms about one-thousandth part. It remains as a residual product when the ore after calcination is treated with hydrochloric acid for the purpose of extracting the cobalt. It is a greyish yellow crystalline powder, mixed with a small quantity of minute dark purple crystals, which are strongly attracted by the magnet, and consist chiefly of magnetic oxide of iron. The crystals of phosphocerite, when examined by the microscope,

* Ann. Ch. Pharm. lvii. 268.

exhibit two forms, one an octohedron, the other, a four-sided prism with quadrilateral summits, both forms apparently belonging to the right prismatic system. Sp. gr. 4·78. The mineral contains 64·68 per cent. protoxide of cerium, &c., 28·46 phosphoric acid, 2·83 oxide of iron, and 3·41 oxide of cobalt, silica, &c. It is very rich in didymium. Strong sulphuric acid, aided by gentle heat, decomposes it, forming a pasty mass, which dissolves in cold water with the exception of a small quantity of silica (Watts).*

ESTIMATION OF CERIUM, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Cerium is precipitated from neutral solutions of cerous salts by potash, as cerous hydrate; or by oxalate of ammonia, as cerous oxalate; and either of these compounds is converted by ignition in an open vessel into ceroso-ceric oxide. This oxide, as already observed, is not perfectly definite in constitution; it may be stated approximately to contain 96·5 per cent. of cerous oxide, or 82·5 per cent. of the metal, and this estimate may be adopted where great accuracy is not required. A more exact method, however, is to dissolve the hydrate precipitated by potash in dilute sulphuric acid, then evaporate, and heat the residue to commencing redness, whereby it is converted into the anhydrous sulphate $CeO . SO_3$, containing 57·6 per cent. of the protoxide of cerium, or 49·6 per cent. of the metal.

Hydrosulphuric acid serves to separate cerium from all metals which are precipitated by that reagent from their acid solutions.

From *manganese, iron, cobalt, nickel, zinc, titanium, chromium, vanadium,* and *tungsten,* cerium may be separated by means of a saturated solution of sulphate of potash.

* Chem. Soc. Qu. J., ii. 131.

From *alumina* it may be separated by carbonate of baryta, which precipitates alumina and not cerous oxide; from *glucina* by sulphate of potash.

From *yttria*, with which it is often associated in minerals, it is separated by a saturated solution of sulphate of potash added in excess, the sulphate of yttria and potash being soluble in excess of sulphate of potash, while the cerous double salt remains undissolved.

From *zirconia*, cerium is separated by treating the boiling acid solution with sulphate of potash, whereby the greater part of the zirconia is precipitated as basic sulphate, while the cerium remains dissolved; to complete the precipitation, a small quantity of ammonia must be added, but not sufficient to saturate the acid (H. Rose).

From *magnesia* also cerium may be separated by sulphate of potash; from *baryta, strontia,* and *lime,* it is separated by ammonia added in slight excess; or from baryta by sulphuric acid, and from strontia and lime by sulphuric acid and alcohol; and from the *fixed alkalies* by precipitation with oxalate of ammonia.

SECTION VI.

LANTHANUM.

Eq. 47, *or* 588; La.

The red-brown oxide obtained from cerite by the methods already described (p. 261), and originally regarded as the oxide of a single metal, cerium, was shown by Mosander *, in 1839, to contain the oxide of another metal, to which he gave the name *lanthanum.* Subsequently, in 1841 †, Mosander discovered that even this supposed simple oxide contained two distinct metals, for one of which the name of lanthanum

* Pogg. Ann. xlvi. 648; xlvii. 207.

† Ibid. lvi. 504.

was retained, while the other was called *didymium.* These two metals appear to be constantly associated with cerium, though not always in the same proportion.

The separation of lanthanum and didymium from cerium may be effected by either of the methods already described (p. 262); the second and third are easier and more expeditious than the first. If the solution obtained by treating the crude red-brown oxide with dilute nitric acid be evaporated to dryness, and the residue treated with nitric acid diluted with at least 200 parts of water, a solution will be obtained quite free from cerium (Marignac). Boiling the red-brown oxide with chloride of ammonium also yields a solution of lanthanum and didymium free from cerium. In both cases, however, it is best to test a portion of the solution for cerium by precipitating with excess of caustic potash, and passing chlorine through the solution. The presence of cerium, even in very small quantity, will be indicated by the formation of a yellow precipitate, after the liquid, supersaturated with chlorine, has been left in a close vessel for several hours.

A solution free from cerium having been obtained, the separation of the lanthanum and didymium is effected by the different solubilities of their sulphates. To convert them into sulphates, the solution is treated with excess of a caustic alkali, and the washed precipitate dissolved in dilute sulphuric acid. The mode of proceeding varies according as the lanthanum or the didymium is in excess.

1. When the lanthanum is in excess, in which case the solution has but a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated in a platinum-dish to a temperature just below redness, to drive off the excess of acid, and render the sulphates perfectly anhydrous. The residue is then dissolved in rather less than six times its weight of water, at about 36° Fah. (2° or 3° C.), the salt being reduced to powder and added in successive small portions,

and the vessel containing the liquid being immersed in ice-cold water. Without these precautions, the temperature of the liquid may be raised several degrees, in consequence of the heat evolved by the combination of the anhydrous sulphates with water; and, in that case, crystallisation will commence, and rapidly extend through the whole mass of liquid, as these sulphates are much less soluble in warm than in cold water; but if the liquid be properly cooled, the whole dissolves completely. The solution is next to be heated in the water-bath to about 104° F. (40° C.); the sulphate of lanthanum then crystallises out, accompanied by only a small quantity of sulphate of didymium. To purify it completely, it is again rendered anhydrous, redissolved in ice-cold water, &c., and the entire process repeated ten or twelve times. The test of purity is perfect whiteness, the smallest quantity of didymium imparting an amethyst tinge (Mosander).

2. When the didymium-salt is in excess, in which case the liquid has a decided rose-colour, separation may be effected by leaving the solution containing excess of acid, in a warm place for a day or two. The sulphate of didymium then separates in large rhombohedral crystals modified with numerous secondary faces; and, at the same time, slender, needle-shaped, violet-coloured crystals are formed, containing the two sulphates mixed. The rhombohedral crystals, which are nearly free from lanthanum, are removed, and the needles, together with the mother-liquid, treated as in the first method, to obtain sulphate of lanthanum (Mosander).

In both cases, the separation may be greatly facilitated by first dissolving the mixed oxides of the two metals in a large excess of nitric acid, and precipitating in successive portions by oxalic acid: the first precipitates thus formed have a much deeper rose-colour, and are much richer in didymium than the latter. The separation thus effected is very imperfect in itself, but it greatly facilitates the subsequent separation of the sulphates, which is much more rapid, when one of the

sulphates is in great excess with regard to the other (Marignac).

Metallic lanthanum is obtained by decomposing the anhydrous chloride with sodium, and dissolving out the chloride of sodium with alcohol of sp. gr. 0·833. It is a dark, lead-grey powder, soft to the touch, and adhering when pressed.

Protoxide of lanthanum, LaO, 55 or 688, is obtained in the anhydrous state by igniting the precipitated hydrate or carbonate in a covered crucible. It is a white powder, which turns brown when heated in the air, probably from partial conversion into a higher oxide. The *hydrated oxide* is formed when the metal or the anhydrous oxide is immersed in warm water, or when a salt of lanthanum is precipitated by caustic potash. It is a white substance, viscid while moist, and slightly alkaline to test-paper. It absorbs carbonic acid from the air with great rapidity.

Oxide of lanthanum, even after strong ignition, dissolves very easily in acids. When boiled with a solution of chloride of ammonium, it dissolves and expels the ammonia. The salts of lanthanum are perfectly colourless when free from didymium. The soluble salts have an astringent taste. *Potash* and *soda,* added to the solutions, throw down the hydrated oxide, which dissolves completely in chlorine-water, without forming any yellow deposit. *Ammonia* throws down a basic salt. *Oxalic acid* or *oxalate of ammonia,* throws down a white flocculent precipitate, which does not become crystalline. In other respects, the solutions resemble those of cerous salts. Compounds of lanthanum do not impart any colour to borax or phosphorus-salt.

Chloride of lanthanum is obtained in the anhydrous state by igniting the oxide in a current of hydrochloric acid gas, and as a hydrate by evaporating a solution of the oxide in hydrochloric acid. It dissolves very readily in water.

Carbonate of lanthanum is found native in small crystalline scales, containing traces of protoxide of cerium. When ob-

tained by precipitation, it forms a gelatinous mass, which gradually changes into shining crystalline scales (Mosander).

Sulphate of lanthanum, $LaO . SO_3$, is obtained by spontaneous evaporation in small prismatic crystals, containing 3 eq. of water of crystallisation. It parts with its water at a low red heat, and with half its acid at a strong red heat. It is much less soluble in hot than in cold water (p. 272). It forms with sulphate of potash a very sparingly soluble double salt, similar to the sulphate of cerium and potassium.

Nitrate of lanthanum crystallises in deliquescent colourless prisms, very easily soluble in water and in alcohol. When carefully heated, so as not to expel any of the acid, it fuses, and solidifies into a colourless glass on cooling. If the heat is raised, so as to drive off a portion of the acid, a fused mass remains which, on cooling, forms a kind of enamel, but almost immediately afterwards crumbles to a bulky white powder, and with such force that the particles are scattered about to a considerable distance (Mosander).

ESTIMATION OF LANTHANUM.

Lanthanum is precipitated from its solutions by potash, or by oxalate of ammonia, and the precipitate converted by ignition in a covered platinum crucible into the anhydrous oxide, containing 85·7 per cent. of the metal.

The methods of separating lanthanum from other metals are the same as those adopted for cerium. The separation of lanthanum from cerium itself may be effected by boiling the mixed oxides in a solution of chloride of ammonium (p. 262).

SECTION VII.

DIDYMIUM.

Eq. 48 *or* 600; Di.

Didymium was discovered by Mosander in 1841*; and its compounds have since been more minutely examined by Marignac.†

A pure salt of didymium is obtained by recrystallising the rose-coloured rhombohedrons which separate from an acid solution of the mixed sulphates of lanthanum and didymium by spontaneous evaporation; and from the pure sulphate thus prepared, the other compounds of the metal may be formed.

Metallic didymium is obtained by heating potassium with an excess of chloride of didymium, and washing out the soluble chlorides with cold water. It is thus obtained, for the most part, as a grey metallic powder; but partly, also, in fused globules. The powder, thrown into the flame of a spirit-lamp, burns with bright sparks like iron-filings. The powder decomposes water at ordinary temperatures; the fused granules do not: in either form, however, the metal dissolves rapidly in dilute acids, with evolution of hydrogen.

Protoxide of didymium, DiO, 56 or 700. — Obtained in the anhydrous state by strongly igniting the nitrate, oxalate, or the precipitated hydrate in a covered crucible. It is perfectly white; is slowly converted into a hydrate by immersion in warm water; dissolves readily in the weakest acids; and expels ammonia from ammoniacal salts when boiled with them. The hydrate, DiO.HO, is a gelatinous mass resembling alumina, but having a very pale rose-colour. It contracts much by desiccation.

* Pogg. Ann. lvi. 504.

† Ann. Ch. Phys. [3], xxxviii. 148; Chem. Soc. Qu. J., vi. 260.

The *salts of didymium* have either a pure rose-colour, like the sulphate, or slightly inclining to violet, like the nitrate in the state of strong solution. *Potash, soda,* and *ammonia* precipitate the hydrate; so does *sulphide of ammonium. Carbonate of baryta* also throws down the hydrated oxide slowly, but completely. *Oxalate of ammonia* precipitates didymium completely from neutral solutions; and *oxalic acid* almost completely, unless the solution contains a large excess of acid. The *sulphates of potash, soda,* and *ammonia* form, immediately in strong, and gradually in weak solutions, rose-white precipitates of double sulphates, slightly soluble in water, less soluble in excess of the reagent; the soda-salt is the least soluble of the three. *Phosphoric* and *arsenic acids,* at a boiling heat, form precipitates sparingly soluble in acids. All compounds of didymium impart to *borax* and *phosphorus-salt* a very pale rose-colour. They do not colour carbonate of soda before the blowpipe.

Peroxide of didymium.—When the oxalate, nitrate, carbonate, or hydrate of didymium is ignited in contact with the air, and not very strongly, a dark brown oxide is obtained, containing from 0·32 to 0·88 per cent. of oxygen more than the protoxide. When treated with acids it dissolves readily, giving off the excess of oxygen, and forming a solution containing the protoxide. It is probably a mixture of the protoxide with a small quantity of a higher oxide of definite composition. By strong ignition in a close vessel, it is converted into the white protoxide.

Sulphide of didymium, DiS, is obtained by igniting the oxide in the vapour of bisulphide of carbon. It is a light, brownish green powder, which dissolves in acids, with evolution of hydrosulphuric acid. A greyish-white *oxysulphide,* 2DiO.DiS, is obtained by igniting the oxide with carbonate of soda and excess of sulphur, and digesting the fused mass in water (Marignac).

Chloride of didymium is obtained as a hydrate in rose-

coloured crystals of considerable size, by evaporating a solution of the oxide in hydrochloric acid. The crystals, which are very soluble in water and alcohol, contain DiCl.4HO. The solution, when evaporated, gives off hydrochloric acid, and leaves an oxychloride, not however of constant composition (Marignac).

Carbonate of didymium, $DiO \cdot CO_2$.—Precipitated as a white, bulky hydrate, tinged with rose-colour, on adding an alkaline carbonate or bicarbonate to a salt of didymium. The precipitate formed in the cold with nitrate of didymium and bicarbonate of ammonia, contains, after drying in *vacuo*, $DiO \cdot Cl_2 + 2HO$. At 212°, it gives off $1\frac{1}{2}$ eq. water and a small quantity of carbonic acid (Marignac).

Oxalate of didymium, $C_4Di_2O_8$, is precipitated from neutral solutions as a rose-white powder, which dissolves in warm nitric or hydrochloric acid, and separates, on cooling, in the form of a granular crystalline powder, sometimes even in small rose-coloured prismatic crystals. After drying in the air, it contains 8 eq. water, 6 eq. of which go off at 212° (Marignac).

Sulphate of didymium, $DiO \cdot SO_3$.—Formed by dissolving the oxide or carbonate in dilute sulphuric acid. The solution is rose-coloured, and deposits, by spontaneous evaporation, dark rose-coloured, shining crystals, having the form of an oblique rhomboidal prism (Mosander), and cleaving readily and distinctly in a direction parallel to the base. They contain $3(DiO \cdot SO_3) + 8$ Aq., and give off the whole of their water at 392° F. (200° C.), leaving an anhydrous powder, which may be heated to redness without further alteration. A solution of the sulphate, when heated, especially to the boiling point, deposits a crystalline precipitate containing $DiO \cdot SO_3 + 2HO$. The following table exhibits the solubility of the anhydrous salt, and of the two crystalline hydrates in water at different temperatures:—

Temperature.	Anhydrous Sulphate.	Sulphate with 2 eq. water.	Sulphate crystallised in the cold.
12° C	43·1	—	—
14	39·3	—	—
18	25·8	16·4	—
19	—	—	11·7
25	20·6	—	—
38	13·0	—	—
40	—	—	8·8
50	11·0	—	6·5
100	—	—	1·7

The anhydrous sulphate, exposed to the heat of an intense charcoal fire, gives off two-thirds of its sulphuric acid, and leaves a *tribasic sulphate*, $3DiO.SO_3$ (Marignac).

Sulphate of didymium, mixed in solution with *sulphate of potash*, forms a crystalline double salt, which appears to contain $KO.SO_3 + 3(DiO.SO_3) + 2HO$; it dissolves in sixty-three times its weight of cold water. With *sulphate of soda* it forms the anhydrous double salt, $NaO.SO_3 + 3(DiO.SO_3)$, which requires two hundred times its weight of water to dissolve it, and is still less soluble in a solution of sulphate of soda. With *sulphate of ammonia*, it forms the salt $NH_4O.SO_3 + 3(DiO.SO_3) + 8HO$, soluble in eighteen times its weight of water (Marignac).

Sulphite of didymium, $DiO.SO_2 + 2HO$.—Oxide of didymium suspended in water, is readily dissolved by a stream of sulphurous acid gas, forming a rose-coloured solution which becomes turbid when heated, forming a light bulky precipitate, which redissolves as the liquid cools, unless the temperature has been raised to the boiling point, in which case it remains undissolved (Marignac).

Nitrate of didymium, $DiO.NO_5$.—This salt is very soluble in water and in alcohol of the strength of 96 per cent. The aqueous solution has a pure rose colour when dilute, but appears violet by reflected light when strong. A syrupy solu-

tion solidifies on cooling into a deliquescent crystalline mass, which, when carefully heated to 300° C., melts, becomes perfectly anhydrous, and exhibits the composition of the neutral nitrate. At a higher temperature, it is decomposed, giving off nitrous fumes, and leaving a residue from which water extracts a portion of neutral nitrate, and leaves a basic salt containing $4DiO.NO_5 + 5HO$. (Marignac).

Phosphate of didymium, $3DiO.PO_5 + 2HO$. — Precipitated, after a few hours, as a white powder, on adding a strong solution of phosphoric acid to a strong solution of nitrate of didymium. It is insoluble in water, very sparingly soluble in dilute acids; but dissolves readily in the stronger acids when concentrated; gives off its water when ignited (Marignac).

Arseniate of didymium, $5DiO.2AsO_5 + 2HO$. — Obtained as a pulverulent precipitate by the action of arsenic acid on solutions of didymium at the boiling heat, or as a gelatinous precipitate by the action of neutral arseniate of potash at ordinary temperatures. It is but slightly soluble in dilute acids (Marignac).

The *quantitative estimation* of didymium is effected in the same manner as that of lanthanum. The anhydrous protoxide contains 85·7 per cent. of the metal.

The methods of separating didymium from the preceding metals are also the same as for lanthanum. For separating it from lanthanum itself, no method has yet been devised sufficiently exact for quantitative analysis.

SECTION VIII.

TANTALUM.

Eq. 68·82 *or* 860·3; Ta.

This metal was discovered by Ekeberg in 1802. It is a rare metal, occurring only in a few minerals, the principal of which are Swedish *tantalite* and *yttro-tantalite*.

Tantalum is obtained, in the metallic state, by heating the fluoride of tantalum and potassium, or fluoride of tantalum and sodium, with sodium, in a well covered iron crucible, and afterwards washing out the soluble salts by water. The reduced metal thus obtained is not quite pure, being more or less contaminated with acid tantalate of soda, the quantity of which may, however, be diminished by covering the mixture in the crucible with chloride of potassium.

Tantalum is a black powder, which, according to H. Rose, is a good conductor of electricity. When heated in the air, it burns with a bright light, and is converted, though with difficulty, into tantalic acid. It is not attacked by sulphuric, hydrochloric, or nitric acid, or even by aqua regia. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum forms two compounds with oxygen, viz., *tantalous acid*, probably TaO, and *tantalic acid*, TaO_2.

Tantalous acid is obtained by placing tantalic acid in a small cavity in a crucible filled with charcoal, and exposing it to the strongest heat of a blast-furnace; a thin film on the outside is at the same time reduced to the state of metal. It is a dark grey mass which scratches glass, and acquires metallic lustre by burnishing.

Tantalic acid, TaO_2; 84·82 or 1060·3.* — This compound is formed when tantalum burns in the air; also by the action of water on chloride of tantalum; and, in the form of a potash-salt, by fusing metallic tantalum or tantalous acid

* The composition of tantalic acid is usually represented by the formula TaO_3, which, according to the original analysis of that compound by Berzelius (88·5 per cent. tantalum + 11·5 per cent. oxygen), gives for tantalum the equivalent number 185. But according to the recent experiments of H. Rose (Berl. Akad. Ber. 1856, 385), the tantalum-compounds appear to contain 2 eq. of the chlorous element, viz., the chloride, $TaCl_2$, tantalic acid, TaO_2, &c.; he also finds the chloride to contain 49·25 per cent. of tantalum, making the equivalent of tantalum 68·82.

with hydrate, carbonate, or bisulphate of potash. It exists, in combination with various bases, in the minerals above mentioned, and is usually extracted from tantalite, which contains the oxides of iron and manganese, together with small quantities of stannic and tungstic acids, by one of the following processes:—1. The mineral, after being pulverised and levigated, is fused with twice its weight of hydrate of potash; the fused mass digested in hot water; and the filtered solution supersaturated with hydrochloric or nitric acid: hydrated tantalic acid is then precipitated in white flakes, which may be purified by washing with water (Berzelius). 2. A better method, however, is to fuse the levigated tantalite in a platinum crucible with six or eight times its weight of bisulphate of potash; pulverise the mass when cold; and boil it repeatedly with fresh quantities of water till no more sulphate of potash, iron, or manganese is dissolved out of it. The residue, which consists of hydrated tantalic acid mixed with ferric oxide, stannic acid, and tungstic acid, is then digested in sulphide of ammonium containing excess of sulphur, which removes the stannic and tungstic acids, and converts the iron into sulphide; the liquid is filtered, and the tantalic acid washed with water containing sulphide of ammonia, then boiled with strong hydrochloric acid to remove the iron, and finally washed with boiling water. The hydrated tantalic acid thus prepared is converted into the anhydrous acid by ignition. It may still, however, contain silica, to remove which, it is dissolved in aqueous hydrofluoric acid, the filtered solution mixed with sulphuric acid and evaporated to dryness, and the residue ignited as long as its weight continues to diminish: the silica is then expelled as gaseous fluoride of silicon (Berzelius).

Anhydrous tantalic acid is a white powder, which remains white when heated, or acquires but a very faint tinge of yellow. Its specific gravity varies from 7·022 to 8·264, increasing with the temperature to which the acid has been

exposed (H. Rose). It neither melts nor volatilises when heated, and is destitute of taste and smell. It is reduced to the metallic state in the circuit of a very powerful voltaic battery; partially also by very strong ignition in contact with charcoal. When ignited in the vapour of bisulphide of carbon, it yields sulphide of tantalum:

$$2TaO_2 + 4CS_2 = Ta_2S_3 + 4CO + 5S.$$

It is insoluble in all acids, and can only be rendered soluble by fusion with hydrate or carbonate of potash.

Hydrated tantalic acid, obtained by precipitating an aqueous solution of tantalate of potash with hydrochloric acid, or by decomposing chloride of tantalum with water containing a small quantity of ammonia, is a snow-white bulky powder, which reddens litmus-paper while moist, and dissolves in hydrochloric and hydrofluoric acids. When strongly heated it gives off its water and becomes incandescent. The hydrate, obtained by fusing tantalite with bisulphate of potash in the manner above described, is of a denser and more crystalline character, is insoluble in all acids excepting strong sulphuric acid, and is precipitated from the solution by water. When heated, it becomes anhydrous, but does not emit light.

Tantalic acid combines with *bases* much more readily than with acids. When fused with *hydrate of potash* in a silver crucible, it forms a transparent mass of tantalate of potash, which, after cooling, dissolves completely in water. With *hydrate of soda* it fuses into an opaque turbid mass, and ultimately deposits a sediment, which is not taken up by fusion with any excess of the alkali. Water poured upon the fused mass when cold dissolves out the excess of soda, but not a trace of tantalic acid; and the residue, when treated with fresh water, dissolves and forms an opalescent solution of acid tantalate of soda, which salt is completely insoluble in a strong solution of caustic soda, and is therefore precipitated on mixing the liquid with the solution of soda previously

obtained by treating the fused mass with water. When tantalic acid is fused with *carbonate of potash* or *soda*, the fused mass is not completely soluble in water.

Hydrochloric acid, added in excess to the solution of an alkaline tantalate, first precipitates the tantalic acid, and then redissolves it, forming a slightly opalescent liquid. *Sulphuric acid* also precipitates the tantalic acid, but does not redissolve it when added in excess. *Carbonic acid gas*, passed through the solution of an alkaline tantalate, precipitates the whole of the tantalic acid in the form of an acid salt. *Chloride* or *sulphate of ammonium* also precipitates the tantalic acid from these solutions in the form of hydrate, mixed with small quantities of ammonia and the fixed alkali. The presence of carbonate of potash or soda prevents the formation of this precipitate at ordinary temperatures; but it then appears after boiling for some time. Sulphide of ammonium produces no precipitate. *Chloride of barium* or *calcium* forms a precipitate of tantalate of baryta or lime, insoluble in water and in ammoniacal salts. *Nitrate of silver* forms, in the solution of a neutral alkaline tantalate, a white precipitate, which is turned brown by a small quantity of ammonia, and dissolves in a larger quantity. A solution of *basic mercurous nitrate* forms a yellowish white precipitate, which turns black when heated. *Ferrocyanide of potassium*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; *ferricyanide of potassium* a white precipitate. *Infusion of galls*, added to a solution of an alkaline tantalate acidulated with sulphuric or hydrochloric acid, forms a light yellow precipitate soluble in alkalies. *Zinc*, immersed in the solution of an alkaline tantalate acidulated with hydrochloric acid, does not produce any blue colour; neither is that colour produced, or but very faintly, on addition of sulphuric acid. But if chloride of tantalum be dissolved in strong sulphuric acid, and then water and metallic zinc added, a fine blue colour is produced, which does

not change to brown, but soon disappears. The blue colour is also produced on placing zinc in a solution of chloride of tantalum in hydrochloric acid, to which a small quantity of water has been added; too much water, however, prevents its formation.

Before the blowpipe, tantalic acid dissolves abundantly in *phosphorus-salt,* forming a clear, colourless glass, which undergoes no alteration when heated in the inner flame, and does not turn red on addition of protosulphate of iron. With *borax* also it forms a transparent glass, which, however, if the quantity of tantalic acid is somewhat large, may be rendered opaque by interrupted blowing, or *flaming,* as it is technically called, but recovers its transparency by long exposure to a continued blast. A very large quantity of tantalic acid renders the glass opaque. No alteration takes place in the inner flame. With *carbonate of soda* on charcoal, tantalic acid produces effervescence, but does not fuse into a bead or undergo reduction.

The above-described characters are sufficient to distinguish tantalic acid from all the substances previously described. From titanic acid, which it most resembles, it is distinguished, first, by its behaviour before the blowpipe; secondly, by its perfect insolubility in strong sulphuric acid after ignition, ignited titanic acid, when finely pulverised, being soluble in that acid; and, thirdly, by the fact that, when it is fused with bisulphate of potash, and the fused mass treated with cold water, the tantalic acid remains undissolved in combination with sulphuric acid; whereas titanic acid, similarly treated, yields a fused mass, which dissolves completely in a considerable quantity of cold water, provided the fusion has been continued long enough. From silica, tantalic acid is distinguished by its behaviour before the blowpipe, silica being insoluble in phosphorus-salt, and fusing to a transparent bead when heated on charcoal with a small quantity of carbonate of soda. The behaviour of tantalic acid with zinc, with tinc-

ture of galls, and with hydrofluoric acid, also distinguishes it from silica.

Sulphide of tantalum, Ta_2S_3. — Obtained by igniting tantalic acid in the vapour of bisulphide of carbon, or by exposing chloride of tantalum to the action of hydrosulphuric acid gas. The product is not perfectly definite in either case. The second process yields a sulphide containing 24·08 per cent. sulphur, whereas the formula Ta_2S_3 requires 25·86 per cent. The former process gives a product containing 28·5 per cent. sulphur. Sulphide of tantalum is a black substance, which acquires a brass-yellow colour by trituration in an agate mortar. Heated in an atmosphere of chlorine gas, it is converted into chloride of tantalum and chloride of sulphur (H. Rose).

Chloride of tantalum, $TaCl_2$.—Prepared by passing chlorine gas over a heated mixture of tantalic acid and charcoal. Tantalic acid is mixed with starch or sugar, and the mixture completely charred by ignition in a covered crucible. It is then introduced in small pieces into a glass tube which is strongly heated by a charcoal fire, while a stream of dry carbonic acid is passed through it. As soon as all the moisture is expelled, the tube is left to cool, the flow of carbonic acid being still kept up; the carbonic acid apparatus is then replaced by a chlorine apparatus, and the tube again heated after the carbonic acid and atmospheric air have been completely expelled by the chlorine. Chloride of tantalum is then obtained in the form of a sublimate of a pure yellow colour. If, however, the tantalic acid contains tungstic acid, the colour of the sublimate is red; and if stannic or titanic acid is present, yellow drops of liquid chloride are also produced. Chloride of tantalum melts at 430°, and volatilises at 291°. Water decomposes it, forming hydrochloric and tantalic acids; but the decomposition is not complete even at the boiling heat: water containing a small quantity of ammonia decomposes the chloride perfectly even at ordinary tempera-

tures. According to the recent experiments of H. Rose, chloride of tantalum contains 81·14 per cent. of tantalum.

Bromide of tantalum is prepared in the same manner as the chloride; when freed from excess of bromine, it has a yellowish colour.

Fluoride of tantalum, TaF_2.—Ignited tantalic acid does not dissolve in aqueous hydrofluoric acid; but the hydrate dissolves, forming a clear solution, which, when evaporated, partly gives off the tantalum as fluoride, but also leaves a white residue of oxyfluoride. Fluoride of tantalum forms with fluoride of potassium a crystalline double salt, containing $KF.2TaF_2$; and with fluoride of sodium the salt, $NaF.TaF_2$ (H. Rose).

ESTIMATION AND SEPARATION OF TANTALUM.

Tantalum is estimated in the form of anhydrous tantalic acid, containing 81·13 per cent. of the metal. It occurs in nature associated with lime, magnesia, yttria, and the oxides of iron and manganese, and occasionally with zirconia, titanic acid, and a few other substances. From these it is separated by fusion with hydrate of potash, or, better, with bisulphate of potash, in the manner already described (p. 279). Some compounds of tantalic acid may be decomposed by sulphuric acid, the tantalic acid being separated in the insoluble state, and all the bases passing into the solution.

Tantalate of *zirconia* may be decomposed in this manner. On treating that compound with strong sulphuric acid, and digesting the cooled mass for some time with a large quantity of water, sulphate of zirconia dissolves, and tantalic acid remains behind in combination with sulphuric acid, from which it may be purified by repeated boiling with water.

From *titanic acid*, with which it sometimes occurs in nature, tantalic acid is separated by fusing the mineral with bisulphate of potash, and treating the fused mass with a large quantity of

water. Titanic acid then dissolves, especially if the water is slightly acidulated with hydrochloric acid, while sulphate of tantalic acid remains undissolved. The titanic acid is precipitated from the solution by boiling: the separation is, however, not very complete. In some cases, the decomposition may be effected by sulphuric acid.

From the *alkalies*, tantalic acid may be completely separated by sulphuric acid, provided the compound is soluble in water. In the contrary case, it must first be fused with carbonate or hydrate of potash. If, however, the quantity of alkali is to be likewise estimated, the compound must be rendered soluble by fusion with sulphate of ammonia.*

SECTION IX.

COLUMBIUM.

Synonyme. Niobium; Cb.

This metal was discovered by Hatchett in 1801, in a black mineral (columbite), from Massachusetts, in North America; it was thence named *Columbium.* Wollaston, in 1809, examined it further, and pronounced it to be identical with the tantalum discovered by Ekeberg, in Swedish tantalite. This idea of the identity of the two metals remained current till 1846, when H. Rose†, by a more careful investigation of the matter, was led to conclude that the American columbite, and the tantalite from Bodenmais, in Bavaria, contained two acids bearing a very close resemblance to tantalic acid, but nevertheless, distinct from it and from each other. To the metals supposed to exist in these acids he assigned the names *Niobium* and *Pelopium.* But by a later investigation‡, he finds that

* H. Rose, Handb. d. Anal. Chem. 1851, ii. 326—335.
† Pogg. Ann. lxiii. 317; lxix. 115.
‡ Pogg. Ann. xc. 456; Ann. Ch. Pharm. lxxxviii. 245.

these two acids really contain the same metal, associated with different quantities of oxygen; he therefore discards the name pelopium, and proposes to designate by *niobium* the metal contained in American columbite and Bavarian tantalite. As, however, this metal is clearly the one discovered fifty years ago by Hatchett, we cannot do better than retain for it the name originally proposed by its discoverer, viz., Columbium.*

Columbium likewise occurs, associated with yttrium, uranium, iron, and small quantities of other metals, in a Siberian mineral called urano-tantalite, yttro-ilmenite, or samarskite; also in pyrochlore, eukolite or wöhlerite, euxenite, and in a variety of pitchblende from Satersdälen.

Metallic columbium is obtained by passing dry ammoniacal gas over the chloride. It is a black powder, which oxidises when heated in the air. Nitric acid and aqua-regia have no effect upon it; but a mixture of hydrofluoric and nitric acids attacks it at ordinary temperatures. It combines with oxygen in two proportions, forming *columbous* and *columbic* acids, formerly supposed by Rose to contain different metals, and called respectively niobic and pelopic acids. The composition of these acids has not yet been determined.

Columbous acid, or a mixture of that acid with columbic acid, is separated from the minerals containing it by processes similar to those already described for the preparation of tantalic acid (p. 279); and when the acid, or mixture of acids, thus obtained, is mixed with charcoal and heated in a stream of chlorine gas, with the precautions already detailed for the preparation of chloride of tantalum (p. 285), it is generally converted into two chlorides,—the one white, volatile, but not fusible; the other yellow, likewise volatile, and easily fusible: the latter contains the larger proportion of chlorine. It was the formation of these two chlorides which led Rose to conclude that certain varieties of tantalite contained two distinct

* See a paper "On the Nomenclature of the Metals contained in Columbite and Tantalite," by Prof. Connell, Phil. Mag. [4].

metals, niobium and pelopium; he now finds, however, that the substance which he regarded as perfectly pure niobic acid, obtained by the action of water on the white chloride, may, by mixing it with a large excess of charcoal, and gently igniting the mixture in a stream of chlorine gas, with strict attention to all the precautions above alluded to, be completely converted into the yellow chloride,—the so-called chloride of pelopium. But if a smaller quantity of charcoal be used, or if the mixture be too strongly ignited during the action of the chlorine, especially at the commencement, the white and less volatile chloride (chloride of niobium), is obtained, as well as the yellow compound.

Columbium appears, then, to be capable of uniting with chlorine in two proportions; and the chlorides thus formed yield, when treated with water, two acids of corresponding constitution, viz., *Columbous* and *Columbic acids*, the latter, which contains the larger proportion of oxygen, being formed from the yellow chloride.

Columbous acid (Rose's niobic acid) may, like tantalic acid, be obtained in the amorphous and the crystalline state, viz., by the rapid or gradual action of water on the chloride. Its specific gravity is lower than that of tantalic acid, and is subject to similar variations. Samples of the acid, prepared from various sources, exhibited, after ignition over a spirit-lamp to the point of incandescence, specific gravities ranging from 4·66 to 5·26; by stronger ignition, the density was diminished. The mean density of the amorphous acid was found to be greater than that of the crystalline in the ratio of 1 to 0·875. The acid is colourless both in the anhydrous and hydrated states, but when heated assumes a yellow colour, much deeper than that of heated tantalic acid. The hydrated acid becomes incandescent during its transition to the anhydrous state.

Columbous acid is decomposed by ignition in a stream of hydrosulphuric acid, and converted into sulphide of colum-

bium. When ignited in ammoniacal gas, it turns black, and yields a large quantity of water.

Columbous acid, after ignition, is insoluble in all acids. The hydrated acid is but very sparingly soluble in hydrochloric acid; so that when an alkaline columbite is precipitated by excess of hydrochloric acid, the filtrate retains only a trace of columbous acid in solution. The hydrated acid dissolves, to a certain extent, in oxalic and in hydrofluoric acid.

The *alkaline columbites* are soluble in water, in solutions of potash and carbonate of potash, but dissolve with great difficulty in excess of soda and carbonate of soda, more sparingly even than tantalate of soda. Columbous acid is precipitated from its alkaline solutions by acids, especially by sulphuric acid, even at ordinary temperatures; whereas the precipitation of tantalic acid requires the aid of heat. Oxalic acid does not affect alkaline columbites; but *carbonic acid* gas precipitates an acid salt soluble in a large quantity of water; *acetic acid* and *sal-ammoniac* also form precipitates. A solution of an alkaline columbite, acidulated with sulphuric or hydrochloric acid, forms a red precipitate with *ferrocyanide of potassium,* bright yellow with the *ferricyanide,* and orange-red with *infusion of galls.* A piece of *zinc,* immersed in the acidulated solution, forms a beautiful blue precipitate, which after a while changes to brown.

Before the blowpipe, especially in the inner flame, columbous acid assumes a greenish yellow colour while hot, but becomes colourless on cooling. With *borax* it forms in the outer flame a colourless bead, which, if the acid is in sufficient quantity, becomes opaque by flaming. In the inner flame, the bead assumes a greyish blue colour, provided it contains a sufficient quantity of acid to produce opacity on cooling. In *phosphorus-salt,* the acid dissolves in large quantity, forming a colourless bead in the outer flame, and in the inner, a violet-coloured, or, if the bead be saturated with the

acid, a beautiful blue bead, the colour disappearing in the outer flame. The addition of protosulphate of iron changes the colour to blood-red. These characters, together with the above-mentioned precipitates, sufficiently distinguish columbous from tantalic acid.

Columbic acid (Rose's pelopic acid) bears a very strong resemblance to tantalic acid, and is intermediate in its properties between that acid and columbic acid. Its specific gravity ranges from 5·5 to 6·7. It appears to be susceptible of three modifications; viz., amorphous, crystalline before ignition, and crystalline after ignition at the heat of a porcelain-furnace. It is insoluble in all acids after ignition. It is precipitated from its alkaline solutions by the same reagents as columbous acid. The precipitate formed by hydrochloric acid redissolves in excess, forming an opalescent solution from which the acid is completely precipitated by sulphuric acid at a boiling heat. The acidulated solutions yield a brownish-red precipitate with *ferrocyanide of potassium,* white with *ferricyanide,* and orange-yellow with *infusion of galls. Zinc* behaves with these solutions in the same manner as with solutions of tantalic acid. A fine blue colour is obtained by treating the yellow chloride of columbium with hydrochloric acid, diluting with water, and adding a piece of zinc.

With *borax* before the blowpipe, columbic acid behaves like tantalic acid. In *phosphorus-salt* it dissolves in large quantity, forming a colourless bead in the outer flame. In the inner flame, the bead assumes a light-brown colour, tinged with violet, the colour disappearing again after a while in the outer flame. The addition of protosulphate of iron changes the brown colour to crimson.

It is remarkable that columbic acid cannot be formed directly from columbous acid, even by the most powerful oxidising agents. It appears, however, to be deprived of a portion of its oxygen by certain reducing agents.

The methods of estimating columbium and separating it from other metals are the same as for tantalum. No method is known of separating columbium from tantalum; but these metals have not hitherto been found occurring together.

Ilmenium. (?) — According to the observations of R. Hermann*, it would appear that Siberian yttrotantalite or yttroilmenite contains a peculiar metal, ilmenium, which forms an acid, ilmenic acid, very closely resembling columbous acid, but nevertheless distinct from it; the chief points of difference being the lower specific gravity, viz., 4·1 to 4·2; the insolubility of the hydrate in hydrochloric acid; and the formation of a compound with sulphuric acid which is decomposed by a large quantity of water, leaving a residue of hydrated ilmenic acid. H. Rose †, however, is of opinion that the supposed ilmenic acid is merely columbous [niobic] acid, more or less impure. The question must, for the present, be regarded as undecided. Rose likewise regards yttroilmenite as identical with urano-tantalite or samarskite.

* J. pr. Chem. xxxviii. 91, 119; xl. 475; lxv. 54.
† Pogg. Ann. lxxi. 157.

ORDER VIII.

METALS WHOSE OXIDES ARE REDUCED TO THE METALLIC STATE BY HEAT (NOBLE METALS).

SECTION I.

MERCURY.

Eq. 100 *or* 1250; Hg.

Mercury, or quicksilver, as it is named from its fluidity, has been known from all antiquity. It is found to a small extent in the metallic state, but its principal ore is the native sulphide *cinnabar*. The most valuable European mines of mercury are, those of Almaden in Spain, and of Idria in Illyria. At Almaden the cinnabar is found in veins, often nearly fifty feet thick, traversing micaceous schists of the older transition period: in Illyria it is disseminated in beds of grit, bituminous schist, or compact limestone of more recent date. The mode of extraction in both these localities, consists in simply roasting the ore in a distillatory apparatus, whereby the sulphur is burned and converted into sulphurous acid, while the mercury is set free in the form of vapour, and condenses in chambers or vessels provided for it.

The arrangement adopted in Illyria is represented in figures 12, 13, 14. A is a large furnace (figs. 12 and 14), on each side of which is a series of condensing chambers, CCCCD. The space V, separated from the fire-place by the perforated arch *n n′*, is filled with the ore in large lumps; smaller pieces are introduced into the next compartment above the arch *pp′*; and on the uppermost arch, *r r′*, are laid a number of earthen capsules, containing the pulverised ore and the mercurial residues of preceding operations. The fire being lighted, and the

Fig. 12.

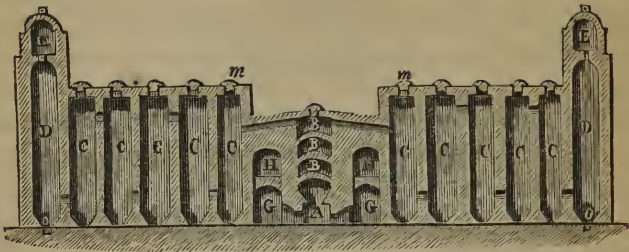


Fig. 13.

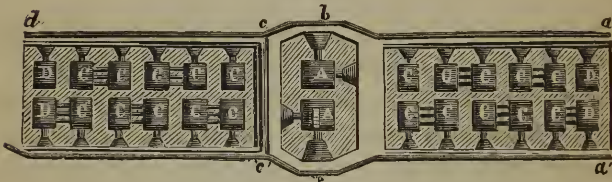
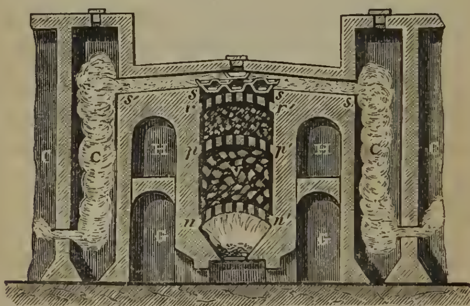


Fig. 14.



heat gradually raised, the sulphur is burned by the air which enters through channels opening into the spaces G, H; and the mixture of mercurial vapour, sulphurous acid, and smoke from the fire, passes through the horizontal channel at the top of the furnace, then up and down through the condensing chambers, C C C C, and finally escapes into the air.

The greater part of the mercury condenses in the first three chambers, whence it runs into the channels $abcd, a'b'c'd'$, which conduct it into a reservoir. To facilitate the condensation of the last portions of mercury in the chambers D D, the vapours are made to pass between a series of boards placed from side to side of these chambers in an inclined position, and having a stream of water continually running over them. As the mercury which condenses in these last chambers is mixed with a considerable quantity of dust, it is collected in separate channels, then filtered, and the residues returned to the furnace as already described.

The mercury obtained by this process is purified by filtration through coarse linen cloth, and sent into the market in wrought-iron bottles, each containing about fifty pounds.

At Almaden, the mercury is also extracted from the cinnabar by roasting, the operation being conducted in furnaces called *buytrones*. (Figs. 15 and 16.)

Fig. 15.

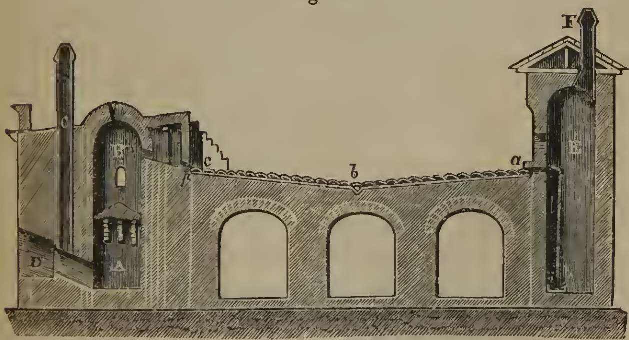
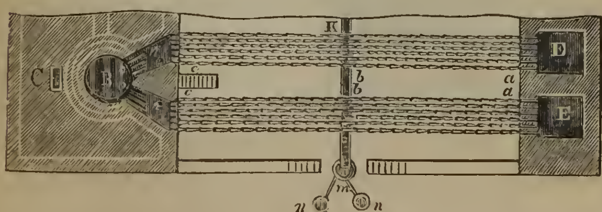


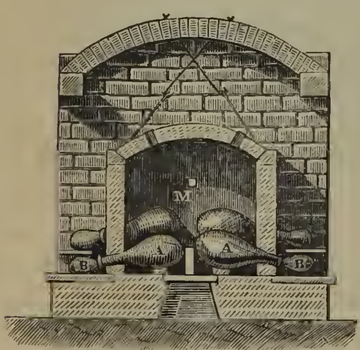
Fig. 16.



The fire is made at A, and the space B, above it, is filled with the ore, the largest pieces being laid on the perforated arch at the bottom, smaller pieces above, and the whole covered with lumps of a mixture of clay, powdered ore, and the residues of preceding operations. The vapours pass through an aperture *p*, in the upper part of the furnace, into a series of tubular vessels called *aludels*, open at both ends and fitting one into the other. These are laid on a surface *c*, *b*, *a*, called the *aludel-bath*, first descending a little, then ascending, and finally opening into the chimney. The form and disposition of the aludels is shown in figure 17. The condensed mercury escapes at the joints of the aludels, and runs into the channel *b b*, by which it is conveyed into the reservoirs *m*, *n n*. The uncondensed mercurial vapour passes into the chamber E, where it deposits a mercurial dust, which yields by filtration an additional quantity of liquid mercury, and a residue which is mixed with clay and pounded ore, and returned to the furnace in the manner above mentioned. The heating of the furnace is continued for twelve or thirteen hours: it is then left to cool for three or four days, after which it is cleared out and arranged for another operation.

Fig. 17.

Fig. 18.



In the duchy of Deux Ponts, a mixture of cinnabar and limestone is heated to redness in retorts of earthenware or cast-iron placed side by side in an oblong furnace (fig. 18),

and provided with receivers containing a certain quantity of water. Sulphide of calcium and sulphate of lime are then formed, and the mercury is evolved in vapour, which condenses in the receivers.

At Horzowitz, in Bohemia, a mixture of cinnabar and smithy-scales is placed in iron dishes, which are attached one above the other by the centres of their bases to a vertical iron axis, and covered with an iron receiver, closed at top and dipping into water at the bottom. The upper part of the receiver is surrounded by the furnace, and imparts its heat to the dishes, from which the mercury rises in vapour and collects in the water below.

The mercury of commerce is generally very pure; it is sometimes, however, contaminated with foreign metals, and in that case its fluidity is remarkably impaired.

Mercury may be purified by distilling it from half its weight of iron-turnings, or by digesting it with a small quantity of nitric acid, or with a solution of corrosive sublimate, which rids it of metals more oxidable than itself. The purification may also be effected by agitating the mercury with a small quantity of solution of sesquichloride of iron. Pure mercury should leave no residue when dissolved in nitric acid, evaporated, and ignited; when made to run down a slightly inclined surface, it should retain its round form, and not *drag a tail;* and when agitated in a bottle with dry air, it should not yield any black powder.

Mercury is liquid at ordinary temperatures. Its colour is white, with a shade of blue when compared with that of silver, and it has a high metallic lustre. At 39° or 40° below zero, it becomes solid, and crystallises in regular octohedrons. According to M. Kupffer, the density of mercury at 39·2° is 13·5886; at 62·6°, 13·5569; and at 78·8°, 13·535 (according to Kopp, it is 13·595 at 39·2°). In the solid state, its density is about 14·0. Mercury boils at 662°, forming a colourless vapour, the density of which was observed, by Dumas, to

be 6976; the theoretical density is 6930. Mercury emits a sensible vapour between 68° and 80°, but not under 20° (Faraday). When heated near its boiling point, mercury absorbs oxygen from the air, and forms crystalline scales of the red oxide. It is not affected by boiling hydrochloric or dilute sulphuric acid, but is readily dissolved by dilute nitric acid. This metal never dissolves in hydrated acids by substitution for hydrogen. Mercury combines with oxygen in two proportions, forming the black oxide, Hg_2O, and the red oxide, composed of single equivalents, HgO, both of which are bases. According to these formulæ, the equivalent of mercury is assumed to be 100; but whether it should be this number or a multiple of it by 2, no certain means exist of deciding, while we are in ignorance of any isomorphous relation of mercury with the magnesian metals.

MERCUROUS COMPOUNDS.

Dioxide of mercury (*black oxide*), *Mercurous oxide*, Hg_2O, 208 or 2600. — This oxide is obtained by the action of a cold solution of potash, used in excess, upon calomel. The substances should be mixed briskly together in a mortar, in order that the decomposition may be as rapid as possible, and the oxide be left to dry spontaneously in a dark place. Mr. Donovan finds these precautions necessary, from the disposition of this oxide to resolve itself into metallic mercury and the higher oxide. The decomposition of mercurous oxide is promoted by elevation of temperature, and by exposure to light.

Mercurous oxide is a black powder, whose density is 10·69 (J. Herapath); it unites with acids and forms salts. Its soluble salts are all partially decomposed by pure water, which combines with a portion of their acid, and throws down a subsalt containing an excess of oxide. They are precipitated black by *hydrosulphuric acid* and *alkaline sulphides*. *Caustic alka-*

lies throw down a black precipitate of mercurous oxide. The *alkaline carbonates* precipitate white mercurous carbonate, which soon turns black from decomposition. *Carbonate of baryta* also decomposes mercurous salts, forming a mercuric salt which remains in solution, and a precipitate of metallic mercury. Mercurous salts are decomposed by *hydrochloric acid* and soluble *chlorides,* with precipitation of calomel as a white powder, a property by which they are distinguished from the salts of the red oxide of mercury. In very dilute solutions, only an opalescence is produced. The precipitate turns black when treated with potash or ammonia. Mercurous salts form with *phosphate of soda* a white precipitate of mercurous phosphate, and with *alkaline chromates,* a brick-red precipitate of mercurous chromate. *Oxalic acid* and *alkaline oxalates* form a white precipitate of mercurous oxalate. *Ferrocyanide of potassium* produces a thick white precipitate, and *ferricyanide of potassium* a red-brown precipitate. *Tincture of galls* yields a brownish-yellow precipitate.

The salts of this, and also of the red oxide, are reduced to the metallic state by copper and the more oxidable metals, and by the proto-compounds of tin; also by phosphorous and sulphurous acids. The precipitated mercury often takes the form of a grey powder, in which no metallic globules are perceptible, and remains in this condition while moist. Mercury in this divided state possesses the medicinal qualities of the milder mercurials, and has often been mistaken for black oxide. To obtain *precipitated mercury,* equal weights of crystallised protochloride of tin (salt of tin) and corrosive sublimate may be dissolved, the first in dilute hydrochloric acid and the second in hot water, and the solutions mixed, with stirring. The salt of tin takes up all the chlorine of the corrosive sublimate, becoming bichloride of tin, which remains in solution, while the mercury is liberated, and forms so fine a precipitate, that it requires several hours to subside. It may be washed by affusion of hot water and subsidence, and

slightly drained on a filter, but not allowed to dry. There can be no doubt that it is in this divided state, and not as the black oxide, that mercury is obtained by trituration with fat, turpentine, syrup, saliva, &c., in many pharmaceutical preparations.

Disulphide of mercury, Hg_2S, is obtained, as a black precipitate, by the action of hydrosulphuric acid on a solution of mercurous nitrate or upon calomel. This sulphide is decomposed by a gentle heat, and resolved into globules of mercury and the higher sulphide.

Dichloride of mercury, Mercurous chloride, Calomel, Hg_2Cl, 235·5 or 2943·75. — A variety of processes are given for the preparation of this remarkable substance. It may be obtained in the humid way, by digesting $1\frac{1}{8}$ parts of mercury with 1 part of pure nitric acid, of density from 1·2 to 1·25, till the metal ceases to dissolve, and the liquid has begun to assume a yellow tint. A solution is also prepared of 1 part of chloride of sodium in 32 parts of distilled water, to which a certain quantity of hydrochloric acid is added; and this, when heated to near the boiling point, is mixed with the mercurial salt. The mercury takes up the chlorine of the common salt, and the subchloride of mercury formed precipitates as a white powder, while the nitric acid and oxygen are given up by the mercury to the sodium, which becomes nitrate of soda:

$$NaCl + Hg_2O \,.\, NO_5 = Hg_2Cl + NaO \,.\, NO_5.$$

The excess of acid in this process is intended to prevent the precipitation of any subnitrate of mercury, which the dilution of the nitrate of mercury, on mixing the solutions, might occasion. Calomel is also obtained by rubbing together, in a mortar, 4 parts of protochloride of mercury (corrosive sublimate) with 3 parts of running mercury. The mixture is afterwards introduced into a glass balloon, and sublimed by a heat gradually increased. Here the protochloride of mercury combines with mercury, and the dichloride is produced. The

same result is obtained by mixing mercuric sulphate with as much mercury as it already contains, and about one-third of its weight of chloride of sodium, and subliming the mixture. The vapour of the dichloride of mercury, in these sublimations, is advantageously condensed by conducting it into a vessel containing hot water; the vapour of the water then condenses the salt in an extremely fine and beautifully white powder. The product of this operation is recommended by its purity, as well as by its minute division; for the water dissolves out all the protochloride of mercury by which the dichloride is accompanied. It appears that whenever the dichloride is sublimed, a small portion of it is resolved into mercury and the protochloride. As the calomel usually condenses in a solid cake, it must, to prepare it for medical use, be reduced to a fine powder, and washed with hot water to remove the soluble chloride.

Dichloride of mercury is obtained by sublimation, in four-sided prisms, terminated by summits of four faces. When the solid cake is finely pounded, the salt acquires a yellow tinge. The density of this salt in the solid condition is 6·5; in the state of vapour 8350. One volume of the vapour contains one volume of vapour of mercury and half a volume of chlorine. This salt is so very sparingly soluble in water, that when mercurous nitrate is added to hydrochloric acid diluted even with 250,000 times its weight of water, a sensible precipitate of dichloride of mercury appears. When boiled for a long time in hydrochloric acid, this salt is resolved into protochloride of mercury which dissolves, and mercury which is reduced.

Action of ammonia on dichloride of mercury.—The dry dichloride was found by Rose to absorb an equivalent of ammonia, and to become black. Exposed to air, the compound loses its ammonia, and the dichloride of mercury recovers its white colour. This ammoniacal compound is

$Hg_2Cl.NH_3$, and may be regarded as $\left.\begin{matrix}\overbrace{NH_3Hg}\\Hg\end{matrix}\right\}Cl$, that is, as dichloride of mercury in which 1 eq. of mercury is replaced by mercurammonium, $\overbrace{NH_3Hg}$. Or again, if we suppose the mercurous salts to contain, not two distinct atoms, but a *double atom* of mercury ($Hg' = Hg_2$), this double atom being the equivalent of one atom of hydrogen — thus, calomel $= Hg'Cl$; black oxide of mercury $= Hg'O$, &c.,— then the ammoniacal compound $Hg_2Cl.NH_3$ may be regarded as *chloride of mercurosammonium*, $\overbrace{NH_3Hg'}.Cl$, or chloride of ammonium in which one eq. H is replaced by a double atom of mercury.

When calomel is digested in aqueous ammonia, it turns black, and was found by Kane to be converted into *mercurous amido-chloride*, $Hg_2Cl.Hg_2NH_2$, sal-ammoniac being formed at the same time:

$$2Hg_2Cl + 2NH_3 = Hg_2Cl.Hg_2NH_2 + NH_4Cl.$$

This compound may also be regarded as *chloride of bimercurosammonium*, $\overbrace{NH_2Hg'_2}.Cl$. It is not altered by boiling water; when quite dry, it is of a grey colour.

Dibromide of mercury, Mercurous bromide, Hg_2Br, is a white insoluble powder, resembling in all respects the dichloride, and formed in similar circumstances. A boiling solution of bromide of strontium was found by Lœwig to dissolve three equivalents of dibromide of mercury, of which one equivalent precipitated during the cooling of the solution. When the filtered solution was evaporated, it deposited a salt in small crystals, containing $SrBr.2Hg_2Br$. These crystals were decomposed by pure water, and resolved into the insoluble dibromide, Hg_2Br, and a double salt, $SrBr.Hg_2Br$, which dissolved easily, and crystallised by evaporation.

Diniodide of mercury, Mercurous iodide, Hg_2I, is obtained by precipitation as a green powder, which is red when heated. It is also formed by triturating mercury and iodine together

in a mortar, with a few drops of alcohol, in the proportion of 2 eq. of the former to 1 eq. of the latter.

No *dicyanide of mercury* exists; and it is doubtful whether a *difluoride*, corresponding with the dioxide, has been formed.

Mercurous carbonate, Carbonate of black oxide of mercury, $HgO_2.CO_2$, precipitates as a white powder, when an alkaline carbonate is added to the nitrate of the same oxide. The precipitate becomes grey when the liquid containing it is boiled, and carbonic acid escapes. This carbonate is soluble both in carbonic acid water, and, to a slight extent, in an excess of alkaline carbonate.

Mercurous sulphate, Sulphate of black oxide of mercury, $Hg_2O.SO_3$; 248 *or* 3100.—This salt is obtained by digesting 1 part of mercury in 1½ parts of sulphuric acid, avoiding a high temperature, and interrupting the process as soon as all the mercury is converted into a white salt. It is also precipitated when sulphuric acid is added to a solution of mercurous nitrate. The salt may be washed with a little cold water. It crystallises in prisms, and requires 500 times its weight of cold and 300 of hot water to dissolve it. With aqueous ammonia this salt forms a dark grey powder, containing ammonia or its elements.

Mercurous seleniate.—Aqueous solutions of seleniate of soda and mercurous nitrate form a white precipitate, probably consisting of the neutral salt, $Hg_2O.SeO_3$, which, however, gradually turns yellow during washing, and, when dried at 100°, is found to be reduced to $6Hg_2O.5SeO_3$ (Körner).

Mercurous selenite.—The neutral salt $Hg_2O.SeO_2$ is found native as *onofrite*, a yellow earthy mineral, occurring, together with horn-quicksilver and native mercury, at San Onofrio, in Mexico. It is also obtained by double decomposition as a white powder, which melts at 356°, and when heated above that point, is converted into a brick-red, opaque, crystalline mass of the salt $3Hg_2O.4SeO_2$ (Köhler).*

* Pogg. Ann. lxxxix. 146.

Mercurous nitrates, Nitrates of black oxide of mercury.—The *neutral nitrate* is obtained when mercury is dissolved in an excess of cold nitric acid: it crystallises readily in transparent rhombs. It is soluble with heat in a small quantity of water, but is decomposed by a large quantity of water, and an insoluble subsalt formed, unless nitric acid be added to the water. The formula of this salt is $Hg_2O.NO_5 + 2HO$. A *subnitrate* is formed when the black oxide is dissolved in a solution of the preceding salt, or when an excess of mercury is digested in diluted nitric acid at the usual temperature. It crystallises readily in white, opaque rhombic prisms, which contain, according to both G. Mitscherlich and Kane, $3Hg_2O.2NO_5 + 3HO$; or, according to Marignac, $4Hg_2O.3NO_3 + HO$. This salt was observed by G. Mitscherlich to be dimorphous. When dissolved by dilute nitric acid, it yields the neutral salt. The subnitrate is soluble in a little water, but when treated with a large quantity, it leaves undissolved, like the neutral nitrate, a white powder, which retains its colour so long as the supernatant liquid is acid, but becomes yellow when washed with water. The *yellow subnitrate of mercury* was found to contain $2Hg_2O.NO_5 + HO$ (Kane). Another subnitrate, containing, according to Marignac, $5Hg_2O.3NO_5 + 2HO$, is obtained by boiling the solution or the mother-liquor of the neutral or the sesquibasic nitrate with excess of mercury for several hours. This salt crystallises in colourless or slightly yellow crystals, derived from an unsymmetrical oblique prism; it appears to be the most stable of all the mercurous subnitrates. When very dilute ammonia is added to the preceding soluble nitrates, without neutralising the whole acid, a velvety black precipitate falls, known as *Hahnemann's soluble mercury*. This salt contains, according to the analysis of C. G. Mitscherlich, $3Hg_2O.NO_5 + NH_3$. But when pains were taken to avoid decomposition of the salt in washing it, its composition was found by Kane to be $2Hg_2O.NO_5 + NH_3$. Bibasic mer-

curous nitrate, mixed in solution with nitrate of lead, yields a crystalline double salt, containing $2(PbO.NO_5)+2Hg_2O.NO_5$; and similar double salts with the nitrates of baryta and strontia (G. Staedeler).

Mercurous acetate, $Hg_2O\,.\,C_4H_3O_3$, falls when acetic acid, or an acetate, is added to the nitrate, in crystalline scales of a pearly lustre. It is anhydrous, and sparingly soluble in water.

MERCURIC COMPOUNDS.

Protoxide of mercury (*red oxide*), *Mercuric oxide*, HgO, 108 *or* 1351.—This compound is formed, as described, by the oxidation of mercury at a high temperature, or by heating the nitrate of mercury till all the nitric acid is expelled, and the mass, calcined almost to redness, no longer emits vapours of nitric oxide. As prepared by the latter process, protoxide of mercury forms a brilliant orange-red powder, crystallised in plates, and having the density 11·074. It is very dark red at a high temperature, but becomes paler as it cools. When reduced to a fine powder, it becomes yellow, like litharge, without any shade of red. It was found by Mr. Donovan to be soluble to a small extent in water, forming a solution which has a slight alkaline reaction. If contaminated with nitric acid, it gives off nitrous fumes when heated in a glass tube, and forms a yellow sublimate of subnitrate. This oxide is known in pharmacy as *red precipitate*. The same compound is obtained by precipitation, when a solution of corrosive sublimate is mixed with an excess of caustic potash; it then forms a dense powder of a lemon-yellow colour. It is necessary to use the potash in excess, otherwise a dark brown oxychloride is formed. The precipitated oxide parts with a little moisture when gently heated, but does not change in appearance. This yellow precipitated oxide differs in some respects from the red oxide; it combines

in the cold with oxalic acid, whereas the red oxide does not; it is converted into black oxychloride by the action of an alcoholic solution of mercuric chloride, which has no action on the red oxide, and it is attacked by chlorine much more readily than the latter. At a red heat, the oxide of mercury is entirely volatilised in the form of oxygen and metallic mercury; the same decomposition takes place more slowly under the influence of light. The oxide detonates when heated with sulphur, and converts chlorine into hypochlorous acid.

The salts of mercuric oxide, when they do not contain a coloured acid, are colourless in the neutral, and yellow in the basic state. They have a disagreeable metallic taste, and act as violent acrid poisons. Some of them, *e.g.* the nitrate and sulphate, are resolved by water into a soluble acid salt, and an insoluble basic salt. From their aqueous solutions the mercury is, for the most part, precipitated in the metallic state by the same substances as from mercurous salts; but the complete reduction of the mercury is often preceded by the formation of a mercurous salt: such, for example, is the action of phosphorous acid, sulphurous acid, protochloride of tin, metallic copper, &c. *Gold* does not by itself reduce mercury from its salts; but if a drop of a mercuric solution be laid on a piece of gold, and a bar of zinc, tin, or iron be brought in contact with the moistened surface, an electrolytic action is set up, and the gold becomes amalgamated at the point of contact. *Hydrosulphuric acid* and *alkaline sulphides*, added in excess to mercuric salts, throw down a black precipitate of mercuric sulphide, insoluble in strong nitric acid. If, however, the quantity of the re-agent added is not sufficient for complete decomposition, a white precipitate is formed consisting of a compound of mercuric sulphide with the original salt, and often coloured yellow or brown by excess of the sulphide: this re-action is quite peculiar to mercuric salts. *Ammonia* and *carbonate of ammonia* form white precipitates,

generally consisting of a compound of the mercuric salt with amide of mercury. The *fixed alkalies* throw down a yellow precipitate of mercuric oxide (not hydrated), insoluble in excess. If, however, the solution contains a large quantity of free acid, no red precipitate is formed, or only a slight one after a considerable time. *Monocarbonate of potash* or *soda* throws down red-brown mercuric carbonate. But if any ammoniacal salt is present in the solution, the fixed alkalies and their carbonates throw down the white precipitate above mentioned. *Bicarbonate of potash* or *soda* also gives a brown-red precipitate, with mercuric nitrate or sulphate; but with the chloride it forms a white precipitate which afterwards turns red. The *carbonates of baryta, strontia,* and *lime* precipitate mercuric oxide from the solutions of the sulphate and nitrate, but not from the chloride. *Phosphate of soda* throws down white mercuric phosphate from the sulphate and nitrate, but not from the chloride. *Chromate of potash* forms a yellowish red precipitate. *Ferrocyanide of potassium* forms, in solutions not too dilute, a white precipitate which gradually turns blue. *Tincture of galls* forms an orange-yellow precipitate with all mercuric solutions except the chloride. *Iodide of potassium* produces a scarlet precipitate of mercuric iodide, soluble in excess either of the mercuric salt or of iodide of potassium.

When aqueous ammonia is digested for several days upon precipitated oxide of mercury, the latter is converted into a yellowish white powder, which Kane regards as $2HgO . HgNH_2 + 3HO$, or as a hydrated compound of amide and oxide of mercury, which may be called oxyamide of mercury. According to Millon*, on the other hand, its composition is $4HgO . NH_3 + 2HO$, or rather $3HgO . HgNH_2 . HO + 2HO$. This substance, when placed in vacuo over quick lime, gives off 2 eq. water, turns brown, and in that state undergoes no further alteration by exposure to the air

* Compt. rend. xxi. 826.

at ordinary temperatures; but between 100° and 130° C., it gives off a third atom of water and is reduced to the anhydrous compound $3HgO . HgNH_2$. The yellow hydrated compound rapidly absorbs carbonic acid from the air, and turns white. Dilute potash has no action upon it; but very strong potash, at a boiling heat, decomposes it, with evolution of ammonia. The brown anhydrous compound resists the action of aqueous potash even at the boiling heat, but is decomposed by fusion with hydrate of potash. Oxyamide of mercury is a powerful base, and expels ammonia from its salts. One equivalent of this compound, represented by the formula $3HgO . HgNH_2$, saturates 1 eq. of sulphuric acid, nitric acid, &c.; thus the sulphate is $3HgO . HgNH_2 . SO_3$; the nitrate, $3HgO.HgNH_2 . NO_5 + HO$, &c. &c.

Nitride of mercury, Mercurammonia, NHg_3. — This compound is formed by passing dry ammoniacal gas over precipitated mercuric oxide previously well washed and dried:

$$3HgO + NH_3 = NHg_3 + 3HO.$$

After removing the excess of mercuric oxide by dilute nitric acid, the mercurammonia is obtained in the form of a dark flea-brown powder, which explodes, by heat, friction, percussion, or by contact with oil of vitriol, almost as violently as iodide of nitrogen. When carefully heated with hydrate of potash, it is decomposed without detonation, yielding ammoniacal gas and sublimed metallic mercury. It is also decomposed by hydrochloric acid, sulphuric, and concentrated nitric acid, yielding an ammoniacal and a mercuric salt. It may be regarded as ammonia in which the hydrogen is entirely replaced by an equivalent quantity of mercury (Plantamour).*

By the action of various ammoniacal salts at a boiling heat on mercuric oxide, compounds are obtained consisting of nitride of mercury combined with mercuric salts: *e.g.* with

* Ann. Ch. Pharm. xl. 115.

nitrate of ammonia, the compound $NHg_3 + 2(3HgO . NO_5)$ is obtained; with *phosphate* of ammonia, the compound $NHg_3 + 3HgO . PO_5 + 2HO$; with *carbonate* of ammonia, the compound $2(NHg_3 + HgO . CO_2 + 2HO) + HO$; with *chromate* of ammonia, the compound $NHg_3 . HgO . 2HO + 4(HgO.CrO_3)$, which when treated with ammonia is converted into $NHg_3 + HgO . CrO_3 + 2HO$; with *acetate* of ammonia, the compound $NHg_3 + C_4H_3HgO_4 + 4HO$, &c. &c. (Hirzel).*

Protosulphide of mercury, Mercuric sulphide, Cinnabar, HgS; 116 *or* 1450. — This is the common ore of mercury, and sometimes occurs crystallised, forming a beautiful vermilion. It is prepared artificially by fusing one part of sulphur in a crucible, and adding to it by degrees six or seven parts of mercury, stirring it after each addition, and covering it to preserve it from contact of air, when it inflames, from the heat evolved in the combination. The product is exposed to a sand-bath heat, to expel the sulphur uncombined with mercury, and afterwards sublimed in a glass matrass at a red heat. A brilliant red mass of a crystalline structure is thus obtained, which, when reduced to fine powder, forms the lively red pigment vermilion. This sulphide is black before sublimation. It is precipitated black also when hydrosulphuric acid is passed through a solution of corrosive sublimate, but is of the same composition in both states. The sulphide of mercury, however, may be obtained of a red colour without sublimation, or in the humid way, by several methods.

Liebig recommends for this purpose to moisten the preparation called white precipitate, recently prepared, with sulphide of ammonium, and allow them to digest together. The black sulphide is instantly produced, which in a few minutes passes into a fine red cinnabar, the colour of which is improved by digesting it at a gentle heat in a strong solution of hydrate of potash. The sulphide of ammonium used in this experiment is prepared by dissolving sulphur to saturation

* Ann. Ch. Pharm. lxxxiv. 258.

in hydrosulphate of ammonia. Cinnabar is not attacked by sulphuric, nitric or hydrochloric acid, or by solutions of the alkalies, but is dissolved by aqua-regia.

Protochloride of mercury, Mercuric chloride, Corrosive sublimate, 135·5 *or* 1693·75. — This compound may be formed by dissolving red oxide of mercury in hydrochloric acid, or by adding hydrochloric acid to any soluble salt of that oxide; but it is generally prepared in a different manner. Four parts of mercury are added to five parts of sulphuric acid, and the mixture boiled till it is converted into a dry saline mass. The mercuric sulphate thus obtained is mixed with an equal weight of common salt, and heated strongly in a retort by a sand-bath; chloride of mercury sublimes and condenses in the upper part and neck of the retort, while sulphate of soda remains behind with the excess of chloride of sodium. The mercury and sodium have exchanged places in the salts:

$$NaCl + HgO \,.\, SO_3 = HgCl + NaO \,.\, SO_3.$$

Mercury, when heated in a stream of chlorine gas, burns with a pale flame, and is converted into a white sublimate of chloride. The salt has been prepared on a large scale in this manner, which was suggested as a manufacturing process by Dr. A. T. Thomson.

The sublimed chloride of mercury forms a crystalline mass, the density of which is 6·5; it fuses at 509°, and boils at about 563°. The vapour of chloride of mercury is colourless, its density 9420, one volume of it containing 1 volume of mercury vapour and 1 volume of chlorine gas. This salt is soluble in 16 parts of cold and in 3 parts of boiling water, in $2\frac{1}{3}$ parts of cold and in $1\frac{1}{6}$ part of boiling alcohol, and in 3 parts of cold ether. It is not decomposed by sulphuric or nitric acid; is largely dissolved by the latter, and also by hydrochloric acid. It is obtained by sublimation and from solution in two different crystalline forms. The solutions of chloride of mercury exposed to the direct rays of the sun

evolve oxygen, while hydrochloric acid is dissolved and dichloride of mercury precipitates. The decomposition of this salt by the action of light is much more rapid when the solution contains organic matter. The poisonous action of chloride of mercury, which is scarcely inferior to that of arsenious acid, is best counteracted by liquid albumen, with which chloride of mercury forms an insoluble and inert compound.

Many metals, viz. arsenic, antimony, bismuth, zinc, tin, lead, iron, nickel, and copper, decompose mercuric chloride in the dry way, withdrawing the half or the whole of its chlorine, and separating calomel or metallic mercury, which latter forms an amalgam with the excess of the other metal. Arsenic forms terchloride of arsenic and a brown sublimate. An intimate mixture of 3 pts. antimony and 1 pt. corrosive sublimate, well pressed into a glass, becomes hot and liquid in the course of half an hour, and on the application of heat yields terchloride of antimony and metallic mercury. Tin heated with corrosive sublimate yields a distillate of bichloride of tin, and a grey residue containing calomel and protochloride of tin. Many metals also reduce the mercury from the aqueous or alcoholic solution of the chloride (p. 306). Most metals throw down calomel together with the mercury; but zinc, cadmium, and iron precipitate nothing but mercury, zinc being thereby converted into a semi-fluid amalgam, and cadmium forming an amalgam which crystallises in beautiful needles. The other reactions of mercuric chloride in solution have been already described (p. 306, 307.).

Chloride of mercury with ammonia.—1. When chloride of mercury is gently heated in a stream of ammoniacal gas, the latter is absorbed, and the compound fuses from heat evolved in the combination. The product was found by Rose to contain $2HgCl . NH_3$. This compound boils at 590°, and may be distilled without loss of ammonia; it is decomposed by water. — 2. *Fusible white precipitate.* When the double

chloride of mercury and ammonium, called sal alembroth, is precipitated by potash in the cold, a white powder is obtained, which was first distinguished by Wöhler from the compound next described; its composition may be expressed, according to Kane's analysis, by the formula $HgCl . NH_3$. The same compound is also formed when ammonia is added to a solution of sal-ammoniac, the liquid brought to the boiling point, and chloride of mercury dropt into it so long as the precipitate which is produced is redissolved. The compound appears, on the cooling of the solution, in small crystals, which are garnet dodecahedrons (Mitscherlich). The crystalline form of this compound belongs, therefore, to the regular system, like that of sal-ammoniac.

3. *Mercuric amido-chloride.*—The compound known as *white precipitate*, and sometimes *infusible white precipitate*, to distinguish it from the preceding, is formed when ammonia is added to a solution of chloride of mercury. When first produced, it is bulky and milk-white; it is decomposed by hot water or by much washing with cold water, and acquires a yellow tinge. Kane has shown that white precipitate is free from oxygen, and contains nothing but the elements of a double chloride and amide of mercury, and represents it by the formula $HgCl . HgNH_2$. White precipitate is distinguished from calomel by solution of ammonia, which does not alter the former, but blackens the latter: it is readily dissolved by acids.

4. *Nitrochloride of mercury.*—Mitscherlich has observed that when white precipitate is gradually heated in a metal bath, and the heat continued for a long time, three atoms of it give off two atoms of ammonia and one atom of chloride of mercury, while a red matter remains in crystalline scales, having much the appearance of red oxide of mercury produced by the oxidation of the metal in air, and containing two atoms of chloride of mercury united with a compound of one atom of nitrogen and three atoms of mercury,

$2HgCl.NHg_3$. He concludes that the atom of white precipitate should be multiplied by three; its decomposition by the heat of the metal bath will then be represented by the equation: —

$$3(HgCl \,.\, HgNH^2) = 2HgCl \,.\, NHg_3 + 2NH_3 + HgCl.$$

The red compound is itself decomposed by a temperature above 680°, and resolved into chloride of mercury, mercury, and nitrogen. It is insoluble in water, and is not altered in boiling solutions of the alkalies. It may be boiled without change in diluted or concentrated nitric acid, and in pretty concentrated sulphuric acid, but it is decomposed and dissolved when boiled in the most concentrated sulphuric acid or in hydrochloric acid; no gas is evolved, but ammonia and chloride of mercury are found in the acid solution. The compound NHg_3 is not isolated by passing ammonia over the heated red compound. Mercury conducts itself in these compounds in the same way as potassium with ammonia, the olive-coloured substance produced by the action of dry ammonia upon potassium being the amide of potassium, $3(K.NH_2)$, and the plumbago-looking substance left on heating the amide of potassium, when ammonia escapes, a compound of nitrogen and potassium, NK_3.*

5. When white precipitate is boiled in water, it is changed into a heavy *canary-yellow powder*, which Kane regards as a compound of the amido-chloride of mercury with oxide of mercury, $HgCl.HgNH_2.2HgO$. Two atoms of water are decomposed in its formation, yielding the two atoms of oxygen which are found in the yellow compound, while the two atoms of hydrogen, added to an atom of chlorine and an atom of amidogen, form an atom of hydrochlorate of ammonia, which is found in solution:

$$2(HgCl.HgNH_2) + 2HO = HgCl.HgNH_2.2HgO + NH_4Cl.$$

* Mitscherlich in Poggendorff's Annalen, vol. xxxix. p. 409.

Solutions of potash and soda convert white precipitate into the same yellow substance, while a metallic chloride is formed and ammonia evolved (Kane).

The five compounds just described may be regarded as salts of metalloïdal radicals formed from ammonium (NH_4) in which the whole or part of the hydrogen is replaced by an equivalent quantity of mercury. Thus, the fusible white precipitate, $HgCl.NH_3$, may be regarded as a *chloride of mercurammonium*, $= Cl.N\left\{\begin{matrix}H_3\\Hg\end{matrix}\right.$; the preceding compound, $2HgCl.NH_3$, as a double chloride consisting of the same compound united with chloride of mercury, namely as $ClHg + Cl.N\left\{\begin{matrix}H_3\\Hg\end{matrix}\right.$; similarly, infusible white precipitate, $HgCl.HgNH^2$, is a *chloride of bimercurammonium*, $ClN\left\{\begin{matrix}H_2\\Hg_2\end{matrix}\right.$; the yellow powder obtained by boiling this compound with water is a *chloride of tetramercurammonium* combined with two atoms of water, $= ClNHg_4 + 2HO$; and the red compound, $2HgCl.NHg_3$, may be regarded as a compound of this same chloride with chloride of mercury, namely as $ClHg.ClNHg_4$.

Oxychloride of mercury.—When a solution of corrosive sublimate is precipitated by potash or soda, mercuric oxide goes down, in combination with a portion of chloride, as a brown precipitate, unless a considerable excess of alkali be employed. The same oxychloride is produced by an alkaline carbonate; but a double carbonate is then also formed. Chloride of mercury is not immediately precipitated by the bicarbonates of potash and soda; and hence that salt may be employed to detect the presence of a neutral alkaline carbonate in these bicarbonates. This oxychloride may also be formed by passing chlorine through a mixture of water and oxide of mercury. It may be obtained crystalline and of a very dark colour, almost black, by mixing corrosive subli-

mate with chloride of lime, and boiling the liquid, or by treating a solution of corrosive sublimate with bicarbonate of potash, and allowing the solution to stand in an open vessel, when carbonic acid gradually escapes, and the compound HgCl . 4HgO is deposited. This oxychloride is decomposed by a moderate heat, chloride of mercury subliming, while the red oxide remains.

Sulphochloride of mercury, HgCl.2HgS. — When hydrosulphuric acid gas is passed through a solution of chloride of mercury, the precipitate which first appears, and does not subside readily, is white; it has been shown by Rose to be a compound of chloride and sulphide of mercury. This substance is changed entirely into sulphide of mercury, when left in water containing hydrosulphuric acid. On the other hand, precipitated sulphide of mercury digested in a solution of chloride of mercury, takes down that salt, and forms the compound in question. The same compound may be formed in the dry way, by fusing protosulphide of mercury (either black or red) with eight or ten times its weight of corrosive sublimate, in a sealed tube, and dissolving out the excess of chloride by boiling water; the sulphochloride then remains *in the form of a dirty-white powder* having a distinctly crystalline structure (R. Schneider). Sulphide of mercury combines likewise with the bromide, iodide, fluoride, and nitrate of mercury, and always in the proportion of two atoms of the sulphide to one atom of the other salt.

Double salts of chloride of mercury.—Chloride of mercury was found by M. Bonsdorff to combine with *chloride of potassium* in three different proportions, forming a series of salts in which the chloride of potassium remains as one equivalent, while the chloride of mercury goes on increasing. They are KCl . HgCl . HO, which crystallises in large transparent rhomboidal prisms; KCl . 2HgCl . 2HO crystallising in fine needle-like amianths; and KCl + 4HgCl + 4HO, which crystallises also in fine needles. *Chloride of sodium* forms only one com-

pound, $NaCl . 2HgCl . 4HO$, which crystallises in fine regular hexahedral prisms. One of the double salts of *chloride of ammonium* has long been known as *sal alembroth.* It crystallises in flattened rhomboidal prisms, $NH_4Cl . HgCl . HO$, and is isomorphous with the corresponding potassium salt. When exposed to dry air, it gives off its water without change of form. Kane has also obtained $NH_4Cl . 2HgCl$, and the same with an atom of water, $NH_4Cl . 2HgCl . HO$, the first in a rhomboidal form, and the second in long silky needles. All these double chlorides are obtained by dissolving their constituent salts together in the proper proportions. The *chlorides of barium* and *strontium* form well-crystallised compounds with *chloride of mercury,* viz. $BaCl . 2HgCl . 4HO$, and $SrCl . 2HgCl . 2HO$. *Chloride of calcium* combines in two proportions with mercuric chloride. When chloride of mercury is dissolved to saturation in chloride of calcium, tetrahedral crystals separate from the solution, which are tolerably persistent in air, and contain $CaCl . 5HgCl . 8HO$. After the deposition of these crystals, the liquid yields, when evaporated by a gentle heat, a second crop of large prismatic crystals, $CaCl . 2HgCl . 6HO$, which are very deliquescent. *Chloride of magnesium* also forms two salts, $MgCl.3HgCl.HO$, and $MgCl.HgCl.6HO$, both deliquescent. *Chloride of nickel* gives two compounds, one of which crystallises in tetrahedrons, like the chloride of calcium salt. *Chloride of manganese* forms a compound in good crystals, $MnCl . HgCl . 4HO$. The *chlorides of iron* and *zinc* form similar isomorphous salts, $FeCl . HgCl . HO$, and $ZnCl . HgCl . HO$. The double chlorides of zinc and of manganese are remarkable in one respect, that chloride of mercury dissolved by them in excess crystallises by evaporation in fine large crystals, such as cannot be obtained in any other way. The *chlorides of cobalt, nickel,* and *copper* form similar crystallisable salts; but chloride of lead does not appear to form a double salt with chloride of mercury. (Bonsdorff.)

Mercuric chloride likewise forms definite compounds with *alkaline chromates.* A hot solution of equal parts of mercuric chloride and *bichromate of ammonia* deposits, on cooling, large hexagonal prisms, of a splendid red colour, containing $NH_4O.2CrO_3+HgCl+HO$, and the mother-liquor deposits a further crop of red, somewhat needle-shaped crystals, containing $3(NH_4O.2CrO_3)+HgCl$. (Richmond and Abel.*) *Monochromate of potash* forms with mercuric chloride a brick-red precipitate of mercuric chromate; and, on evaporating the filtered liquid, small pale red crystals are obtained of a double salt, containing $KO.CrO_3+HgCl$. A solution of equivalent quantities of mercuric chloride and *bichromate of potash* yields beautiful red pointed crystals, containing $KO.2CrO_3+HgCl$. (Darby.†) On mixing the cold saturated aqueous solutions of *acetate of copper* and mercuric chloride, and leaving the mixture to evaporate, deep blue, concentric, radiated hemispheres are obtained, containing $CuO.C_4H_3CuO_4+HgCl$. (Wöhler and Hütteroth.)‡

Protobromide of mercury, Mercuric bromide, HgBr; 180 or 2250.—This salt is obtained by treating mercury with water and bromine. It is colourless, soluble in water and alcohol, and when heated, fuses and sublimes, exhibiting a great analogy to chloride of mercury in its properties. Its density in the state of vapour is 12370. Bromide of mercury forms a similar compound with sulphide of mercury $HgBr.2HgS$, which is yellowish. It was also combined, by Bonsdorff, with a variety of alkaline and earthy bromides. Bromide of mercury combines with half an equivalent of ammonia, in the dry way, and also gives, with solution of ammonia, a white precipitate, analogous to that derived from chloride of mercury.

Protiodide of mercury, mercuric iodide, HgI, 226·36 *or*

* Chem. Soc. Qu. J. iii. 202.
† Chem. Soc. Qu. J. i. 24.
‡ Ann. Ch. Pharm. liii. 142.

2829·5.—Falls as a precipitate of a fine scarlet colour, when iodide of potassium is added to a solution of chloride of mercury. It may also be obtained by triturating its constituents together, in the proper proportion, with a few drops of alcohol. To procure it in crystals, Mitscherlich dissolves iodide of mercury to saturation, in a hot concentrated solution of the iodide of potassium and mercury, and allows the solution to cool gradually. When heated moderately, mercuric iodide becomes yellow; at a higher temperature, it fuses and sublimes, condensing in rhomboidal plates of a fine yellow colour. The forms of the red and yellow crystals are totally different, so that the change of colour is due to the dimorphism of mercuric iodide. The yellow crystals generally return gradually into the red state when cold; and this change may be determined at once by scratching the surface of a crystal, or by crushing it. The density of mercuric iodide in the state of vapour is 15630; it is the heaviest of gaseous bodies. Mercuric iodide is slightly soluble in water, but requires more than 6000 times its weight of water to dissolve it. It is much more soluble in alcohol and in acids, particularly with the assistance of heat. Mercuric iodide is very soluble in iodide of potassium; it is also dissolved by a solution of mercuric chloride, especially when hot. Hence, when a few drops of iodide of potassium solution are added to a solution of corrosive sublimate, a precipitate is formed, which redissolves on agitating the liquid; a somewhat larger quantity of iodide of potassium renders the precipitate permanent; and a still further addition causes it to disappear entirely.

When treated with sulphuretted hydrogen water, mercuric iodide forms the compound HgI . 2HgS, which is yellow. Mercuric iodide unites with other iodides, and forms a class of salts as extensive as the compounds of chloride of mercury. They have been studied by M. P. Boullay.* Mercuric iodide

* Ann. Ch. Phys. [2], xxxiv. 337.

also combines with chlorides; it is dissolved by a hot solution of mercuric chloride, and two compounds have been obtained on the cooling of the solution, viz., a yellow powder, $HgI.HgCl$, and white dendritic crystals, $HgI.2HgCl$.

Mercuric iodide treated with very strong aqueous ammonia forms the compound $\overbrace{NH_3Hg}.I$; with somewhat less concentrated ammonia it yields white needles of the compound $NH_3.2HgI$ or $\overbrace{NH_3HgI}+HgI$, and a red-brown powder consisting of iodide of tetramercurammonium with 2 eq. water NHg_4I+2HO. The formation of this last compound is represented by the equation:

$$4HgI + 4NH_3 + 2HO = NHg_4I.2HO + 3NH_4I.$$

Iodide of tetramercurammonium is also formed by passing ammoniacal gas over mercuric oxy-iodide:

$$HgI.3HgO + NH_3 = NHg_4I.2HO + HO;$$

by digesting the chloride of tetramercurammonium in aqueous iodide of potassium (Rammelsberg); and by adding ammonia to a solution of iodide of mercury and potassium mixed with caustic potash (Nessler *):

$$4(HgI.KI)+NH_3+3KO=NHg_4I.2HO+7KI+HO.$$

This last reaction affords an extremely delicate test for ammonia. A solution of iodide of mercury and potassium is prepared by adding iodide of potassium to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained produces a brown precipitate with a very small quantity of ammonia, either free or in the form of an ammoniacal salt. The precipitate is soluble in excess of iodide of potassium (Nessler).

* Chem. Gaz. 1856, 445. 463.

Mercuroso-mercuric iodide, Hg_4I_3 or $Hg_2I \cdot 2HgI$.—This compound is obtained by precipitating a solution of mercurous nitrate with hydriodic acid or iodide of potassium, and collecting the precipitate on a filter after the green colour has changed to yellow; or by dissolving in aqueous iodide of potassium half as much iodine as it already contains, and adding the solution to a solution of mercurous nitrate. It is a yellow powder, which turns red when heated.

Cyanide of mercury, HgCy, 126 *or* 1575.—This salt is most easily obtained by saturating hydrocyanic acid with red oxide of mercury. To prepare the hydrocyanic acid required, the process of Winkler may be followed. Fifteen parts of ferrocyanide of potassium are distilled with 13 parts of oil of vitriol diluted with 100 parts of water, and the distillation continued by a moderate heat nearly to dryness. The vapour should be made to pass through a Liebig's condensing tube, and be afterwards received in a flask containing 30 parts of water. A portion of the condensed hydrocyanic acid is put aside, and the remainder mixed with 16 parts of oxide of mercury in fine powder, and well agitated till the odour of hydrocyanic acid is no longer perceptible. The solution is drawn off from the undissolved oxide of mercury, and the reserved portion of hydrocyanic acid mixed with it. The last addition is necessary to saturate a portion of oxide of mercury, which cyanide of mercury dissolves in excess. This operation yields 12 parts of the salt in question.

Cyanide of mercury may also be obtained by boiling 1 pt. of ferrocyanide of potassium for ten minutes with 2 pts. of neutral mercuric sulphate and 8 pts. of water, filtering the liquid, and leaving it to crystallise by cooling. The reaction may be represented by the equation:

$$K_2FeCy_3 + 3HgO = 3HgCy + 2KO + FeO.$$

A third method of preparing this compound is to heat the red oxide of mercury with about an equal weight of pure and

finely pounded Prussian blue, and a large quantity of water, stirring the mixture frequently; then boil the filtrate with oxide of mercury to throw down the last portions of iron; and neutralise the excess of mercuric oxide in the liquid with hydrocyanic acid.

Cyanide of mercury crystallises in square prisms which are anhydrous, and resembles chloride of mercury in its solubility and poisonous qualities. The red oxide of mercury, even when dry, absorbs hydrocyanic acid, with formation of water and evolution of heat. The affinity of mercury for cyanogen appears to be particularly intense, oxide of mercury decomposing all the cyanides, even cyanide of potassium, and liberating potash. Cyanide of mercury is consequently not precipitated by potash. Nor is it decomposed by any acid, with the exception of hydrochloric, hydriodic, and hydrosulphuric acids. By a heat approaching to redness, cyanide of mercury is decomposed, and resolved into mercury and cyanogen gas. When exposed in the moist state to the action of chlorine in a dark place, it is converted into mercuric chloride and gaseous chloride of cyanogen:

$$HgCy + 2Cl = HgCl + CyCl.$$

But in strong sunshine, a different action takes place, attended with considerable rise of temperature, and yielding sal-ammoniac, mercuric chloride, a peculiar yellow oil, a small quantity of gaseous chloride of cyanogen, and a trace of carbonic acid (Serullas). When hydrocyanic acid is digested upon mercurous oxide, the mercuric cyanide dissolves, and metallic mercury is liberated.

Oxycyanide of mercury, $HgCy.HgO$, is produced as a white powder intermixed with the red oxide, when hydrocyanic acid of considerable strength (10 or 20 per cent.) is agitated with red oxide of mercury in large excess. It is sparingly soluble in cold water, but may be dissolved out by hot water, and crystallises on cooling in transparent, four-sided, acicular

prisms. When heated gently, it blackens slightly, and then explodes (Johnston).*

Cyanide of mercury, digested upon red oxide of mercury, dissolves a large quantity of it, and forms, according to Kühn, a *tribasic cyanide of mercury*, $HgCy . 3HgO$, which is more soluble in water than the neutral cyanide, and crystallises with less facility in small acicular crystals.

Cyanide of mercury and potassium, $KyCy . HgCy$, is formed on dissolving cyanide of mercury in a solution of cyanide of potassium, and crystallises in regular octohedrons. Cyanide of mercury also forms crystallisable double salts with other cyanides, such as the cyanides of sodium, barium, calcium, magnesium, &c. It also combines with chlorides, bromides, iodides, and with several oxi-salts, such as chromate and formiate of potash, with which it forms the compounds $2(KO . CrO_3) + HgCy$ and $C_2HKO_4 . HgCy$.

Mercuric sulphate, $HgO . SO_3$; 148 *or* 1850.—This salt is formed by boiling 5 parts of sulphuric acid upon 4 parts of mercury, till the metal is converted into a dry saline mass. Mercuric sulphate is a white crystalline salt, neutral in composition, but, like most of the neutral salts of mercury, cannot exist in solution. Water decomposes it, forming a dense yellow subsulphate, and a solution of an acid sulphate. This subsulphate is known as *turbith mineral*, a name applied to it by the older chemists, because it was supposed to produce effects in medicine analogous to those of a root formerly employed, and known as convolvulus turpethum. The composition of turbith mineral is $3HgO . SO_3$ or $HgO . SO_3 + 2HgO$ (Kane). Solution of ammonia converts both the neutral sulphate and turbith mineral into a heavy powder, which Kane names *ammonio-turbith*, and finds to be $HgO . SO_3 + Hg . NH_2 + 2HgO$. It is, therefore, analogous in composition to the yellow powder produced by the decomposition of white pre-

* Phil. Trans. 1839, p. 113.

cipitate, and may be regarded as a sulphate of tetramercurammonium with 2 eq. water: $NHg_4 . SO_4 + 2HO$.

Mercuric sulphites.—The neutral sulphite, $HgO . SO_2$, may be formed by precipitating the nitrate, $HgO . NO_5$, with an alkaline sulphate; but it is very unstable, and resolves itself spontaneously into mercuric sulphate and metallic mercury. The *basic sulphite*, $2HgO . SO_2$, is obtained by precipitating a solution of the basic nitrate, $2HgO . NO_5$, with an alkaline sulphite. It is a white, heavy powder, insoluble in water, and changing, when slightly heated, into mercurous sulphate; $2HgO . SO_2 = Hg_2O . SO_3$. Iodide of potassium converts it into red mercuric iodide (Péan de St. Gilles).* A *bisulphite*, $HgO . 2SO_2 + HO$, is obtained as a white crystalline powder by pouring a saturated solution of bisulphite of soda on solid mercuric chloride. It dissolves readily in water, and is decomposed by heat, whether in solution or in the solid state, with separation of metallic mercury (Wicke).† By treating mercuric chloride with a solution of neutral sulphite of potash, a double salt, $HgO . SO_2 + HO$, is obtained in small needle-shaped crystals, whose solution is neutral to test-paper. Similar salts are formed with the neutral sulphites of soda and ammonia. By treating mercuric chloride in excess with neutral sulphite of soda, the salt, $2(HgO . SO_2) + NaO . SO_2 + HO$, is obtained, which is alkaline to test-paper. The solutions of these double sulphites are precipitated by hydrosulphuric acid and soluble sulphides, but not by alkalies. (Péan de St. Gilles.)

Mercuric seleniate.—A hot aqueous solution of selenic acid forms with mercuric oxide prepared by precipitation, a soluble neutral seleniate, $HgO . SeO_3 + HO$, and a red insoluble basic salt, containing $2(3HgO . SeO_3) + HO$ (Körner).‡

Mercuric selenite.—Mercuric oxide forms with aqueous

* Ann. Ch. Phys. [3], xxxvi. 80.
† Ann. Ch. Pharm. xcv. 176.
‡ Pogg. Ann. lxxxix. 146.

selenious acid, according to Berzelius, an insoluble neutral and a soluble acid selenite; according to Köhler, on the other hand, selenious acid does not form any soluble salt with mercuric oxide, but only a pale yellow amorphous salt, containing $7HgO . 4SeO_2$.

Nitrates of the red oxide of mercury, Mercuric nitrates.—The neutral nitrate cannot be crystallised, but it is formed in solution when chloride of mercury is precipitated by nitrate of silver. When red oxide of mercury is dissolved in nitric acid, or when the metal is dissolved in the same acid with ebullition, till a drop of the solution no longer occasions a precipitate in water containing a soluble chloride, a subnitrate is formed, crystallising in small prisms, which are deliquescent in damp air. Its composition is expressed by the formula $2HgO . NO_5 + 2HO$. It is the only crystallisable nitrate of this oxide. Decomposed by water, this salt yields a yellow subnitrate, which, after washing with warm but not boiling water, is $3HgO . NO_5 + HO$. When the subnitrate is prepared by boiling water, it has a red colour, and probably consists of $6HgO . NO_5$ (Kane).

Nitrate of mercury yields several compounds when treated with ammonia. (*a.*) When a dilute and not very acid solution of that salt is treated in the cold, with weak solution of ammonia not added in excess, a pure milk-white precipitate appears, which is not granular, and remains suspended in the liquid for a considerable time. It was analysed by C. G. Mitscherlich, and to distinguish it from some other salts containing the same constituents, may be called *Mitscherlich's ammonia-subnitrate.* It contains $2HgO . NO_5 + HgNH_2$. (*b.*) The preceding compound is altered in its appearance by boiling water, and becomes much heavier and more granular, forming *Soubeiran's ammonia-subnitrate,* the composition of which is found by Kane to be $HgO . NO_5 + Hg . NH_2 + 2HgO$, or it resembles in constitution the bodies already described containing chlorine and sulphuric acid. This compound is

also formed by decomposing a dilute solution of mercuric nitrate with a slight excess of ammonia (Soubeiran). (*c.*) A third compound, the *yellow crystalline ammonia-subnitrate,* was obtained by C. G. Mitscherlich by boiling the ammonia subnitrate (*a*) with excess of ammonia, and adding nitrate of ammonia, by which a portion of the powder is dissolved; the solution, as it cools and loses ammonia, yields small crystalline plates of a pale yellow colour. The constituents of this salt are $2HgO . NO_5$ and NH_3. Kane doubles its equivalent, and represents it as a compound of Soubeiran's salt with nitrate of ammonia, as it appears to be produced by the solution of the former salt in the latter, $(HgO . NO_5 + Hg . NH_2 + HgO) + NH_4O . NO_5$. (*d.*) Soubeiran's ammonia subnitrate (*a*) is dissolved in considerable quantity, when boiled in a strong solution of nitrate of ammonia, and the solution deposits, on cooling, small but very brilliant needles, which were observed and analysed by Kane. This salt, which may be called *Kane's ammonia subnitrate,* is decomposed by water, nitrate of ammonia dissolving, and Soubeiran's subsalt being left undissolved. It contains the elements of $3(NH_4O . NO_5)$ and $4HgO$. Kane believes that it is most likely to contain Soubeiran's subnitrate ready formed, which leaves two atoms of nitrate of ammonia and two atoms of water to be otherwise disposed of.*

These ammonia-nitrates, like the corresponding chlorides and sulphates, may be regarded as nitrates of mercurammoniums, containing one or more atoms of mercury in place of hydrogen. Thus, Mitscherlich's ammonia-subnitrate (*a*) is $\overbrace{NHHg_3} . NO_6 + HO$ = nitrate of trimercurammonium with 1 eq. water; Soubeiran's salt (*b*) is $NHg_4 . NO_6 + 2HO$= nitrate of tetramercurammonium with 2 eq. water; the crystalline salt (*c*) is $\overbrace{NH_2Hg_2} . NO_6 + HO$ = nitrate of bimercurammonium with 1 eq. water; and (*d*) is a compound of (*b*)

* Trans. of the Royal Irish Academy, vol. xix. pt. i.; or, Ann. Ch. Phys. [2], lxxii. 225.

with nitrate of ammonia and water = $2(NH_4.NO_6)+2HO+(NHg_4.NO_6+2HO)$.

Nitrate of mercury forms an insoluble compound with sulphide of mercury, $HgO.NO_5+2HgS$, resembling the compounds of the sulphate and chloride with sulphide of mercury. It also forms double salts with iodide and cyanide of mercury.

Alloys of mercury or amalgams.—Mercury combines with a great number of metals, forming compounds called *amalgams*, which are liquid or solid according as the mercury or the other metal predominates. A very small quantity of a foreign metal suffices to impair the fluidity of mercury in a very great degree. All amalgams are decomposed by heat, the mercury volatilising and the other metal remaining.

The union of mercury with potassium and sodium is attended with considerable disengagement of heat; the resulting amalgams are of a pasty consistence, and decompose water. The amalgams of tin and lead, when heated till they are quite liquid, and then left to cool slowly, yield solid crystalline amalgams of definite constitution. An amalgam of silver, Hg_2Ag, is found native in the form of regular dodecahedrons.

An amalgam of tin is used for *silvering* glass. For this purpose a sheet of tinfoil is laid on a horizontal table, and mercury poured over the whole surface, so as to form a layer about 1-5th or 1-6th of an inch thick. The plate of glass is then slid along the surface in such a manner as to cut this layer in halves horizontally, which prevents the introduction of air-bubbles. The glass is then loaded with weights, so as to press out the excess of mercury; and after a few days, the surface is found to be covered with a closely-adhering layer of an amalgam containing about 5 parts of tin to 1 of mercury.

Mercury combines very readily with bismuth. An amalgam obtained by heating a mixture of 497 parts of bismuth,

310 lead, 177 tin, and 100 mercury, is very well adapted for injecting anatomical preparations: it is solid at ordinary temperatures, and has a silvery lustre, melts at 171·5 (Fah.), and solidifies at 140°. An amalgam of lead and tin, sometimes also containing bismuth, is used for covering the cushions of electrical machines.

ESTIMATION OF MERCURY, AND METHODS OF SEPARATING IT FROM THE PRECEDING METALS.

Mercury is generally estimated in the metallic state; sometimes, however, as sulphide, HgS, or as dichloride, Hg_2Cl. To separate it from its compounds in the metallic state, it may be distilled with quicklime, in a tube of hard glass sealed at one end. Into this tube is introduced, first a layer of carbonate of lime, about an inch long; then the mixture of the substance with quicklime; lastly, a layer of quicklime about two inches long, and a plug of asbestos to keep the lime in its place. The open end of the tube is next drawn out into a narrow neck, and bent at an obtuse angle. The tube is laid in a combustion-furnace, the same as that which is used for organic analysis (I, 373), the neck being turned downwards and made to pass into a narrow-mouthed bottle containing water, so as to terminate just above the surface of the water. The tube is then gradually heated by laying pieces of red-hot charcoal round it, beginning at the part near the neck, containing the pure quicklime. This portion having been brought to a full red heat, the heat is carefully extended towards the middle part, to decompose the compound and volatilise the mercury: any portion of the compound that may volatilise undecomposed, will be decomposed in passing over the red-hot lime at the end. Lastly, the back part of the tube containing the carbonate is heated, so as to evolve carbonic acid gas and sweep out all the mercury vapour contained in the tube. The quantity of carbonic acid thus

evolved may be increased by mixing the carbonate of lime with bicarbonate of soda. The mercury condenses under the water in the bottle, which must be kept cold. The water is poured off as completely as possible; the mercury transferred to a weighed porcelain crucible; the greater part of the water which still adheres to it removed by means of blotting-paper; the drying completed over sulphuric acid; and the mercury finally weighed.

Mercury may also be precipitated from its solutions in the metallic state by protochloride of tin, or by phosphorous acid; the solution then decanted; the mercury washed with water; and dried in the manner just described.

Mercury is also frequently precipitated from its solutions, as a sulphide, by hydrosulphuric acid. In that case, if the precipitate consists of the pure protosulphide, HgS, as when it is thrown down from a solution of corrosive sublimate, the precipitate may be simply collected on a weighed filter, washed, dried over the water-bath, weighed, and the quantity of mercury thence determined. But if, as is generally the case, the precipitate also contains free sulphur, as when it is thrown down from a solution containing a ferric salt, or a considerable excess of nitric acid,—or if it be precipitated in conjunction with the sulphides of other metals, then the mercury must be separated from it by distillation with lime, as above described. Or again, the mixture of sulphides may be converted into chlorides by gentle heating in a stream of chlorine gas, the volatile chloride of mercury passed into water, and the mercury precipitated from the solution by protochloride of tin.

The precipitation of mercury in the form of dichloride is best effected by means of hydrochloric acid and formiate of potash or soda. If the mercury is contained in an alloy, the alloy must be dissolved in aqua-regia; if it is contained in solution in the form of mercuric nitrate, hydrochloric acid must be added, the solution, in either case, nearly neutralised

with potash, formiate of potash or soda then added, and the whole exposed for some days to a temperature between 140° and 176° F. (at the boiling heat, the mercury would be reduced to the metallic state.) The dichloride then precipitates, and must be collected on a weighed filter, washed, dried at a gentle heat, and weighed.

The quantity of *mercurous oxide* present in a solution may also be determined by precipitation with hydrochloric acid. The solution must, however, be very dilute, and be kept cool; it must also contain but a very small quantity of free nitric acid, as a larger quantity would convert the dichloride of mercury into protochloride. To determine the proportions of mercurous and mercuric oxide, when they exist together in solution, the mercurous oxide is first precipitated with hydrochloric acid, and the remaining mercury by protochloride of tin or hydrosulphuric acid.

Mercury may be separated from all other metals, except arsenic and antimony, by its superior volatility. When it exists in the form of an amalgam, the compound is simply heated, and the quantity of mercury determined by the loss of weight. If it exists as an oxide, chloride, &c., combined with compounds of other metals, it may be separated by distillation with quicklime, as above described. Its separation from the *alkalies* and *earths,* and from *uranium, manganese, nickel, cobalt, iron, zinc,* and *chromium,* may also be effected by precipitation with hydrosulphuric acid. From *bismuth* and *cadmium* it may be separated by reduction with protochloride of tin; from *copper,* by mixing the solution with excess of cyanide of potassium, and passing hydrosulphuric acid through the liquid, whereby the mercury is precipitated as sulphide, while the copper remains dissolved; from *lead,* by precipitating that metal with sulphuric acid; also by treating the solution with excess of cyanide of potassium, which precipitates the lead, but not the mercury. From *arsenic, tin* and *antimony,* mercury is separated by the solubility of the sulphides of those metals in sulphide of ammonium.

SECTION II.

SILVER.

Eq. 108, *or* 1350; Ag (*argentum*).

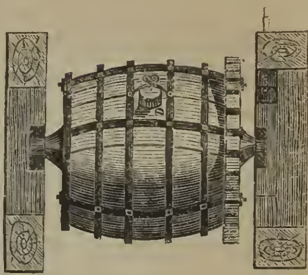
This metal is found in various parts of the world, and occurring often in the metallic state, and being easily melted, must have attracted the attention of mankind at an early period. Before the discovery of America, the silver mines of Saxony were of considerable importance; but the silver mines of Mexico and Peru far exceed in value the whole of the European and Asiatic mines, the former having furnished during the last three centuries, according to Humboldt, 316 millions of pounds troy of pure silver.

A considerable quantity of silver is obtained from ores of lead by cupellation, as described under that metal. From argentiferous copper ores also the silver is extracted by a process called *liquation*, which consists in fusing the *coarse copper* (p. 93.) with three times its weight of lead; a mixture of two alloys is then obtained, the more fusible of which, containing the greater part of the lead and nearly all the silver, is separated by the application of a moderate heat, and yields the silver by cupellation.

Native silver, which is in the form of threads or thin leaves, is separated from the gangue or accompanying rock, by *amalgamation*, a process which is also followed in the treatment of the most frequent ore of silver, the sulphide, when it is not accompanied by sulphide of lead. At Freiberg, in Saxony, the sulphide of silver, ground to powder, is roasted in a reverberatory furnace with 10 per cent. of chloride of sodium, by which the silver is converted into chloride. It is then introduced into barrels (fig. 19.), with water, iron, and a quantity of metallic

mercury, and the materials kept in a state of agitation for eighteen hours by the revolution of the barrels on their axes. The chloride of silver, although insoluble, is reduced to the metallic state by the iron, and chloride of iron is produced, while the silver forms a fluid compound with the mercury. By adding more water, and turning the barrels more slowly, the fluid amalgam separates and subsides. It is drawn off and subjected to pressure in a chamois leather bag, the mercury passing through the leather, while a soft amalgam of silver remains in the bag. The mercury is afterwards separated from this amalgam by a species of distillation, *per descensum,* and the silver remains.

Fig. 19.



In South America, where fuel is scarce, a different process is adopted. The ore, in a finely divided and moist condition, is exposed for a considerable time to the successive action of common salt, sulphate of copper (obtained by roasting copper pyrites), and mercury, the materials being spread on a paved floor, and trodden by men or horses to effect an intimate mixture; and the silver amalgam thus obtained is separated from the exhausted ore by washing with water. In this process, the chloride of sodium and sulphate of copper form sulphate of soda and protochloride of copper. The latter gives up chlorine, converting part of the silver into chloride, and separates the sulphur, provided an excess of chloride of sodium is present to dissolve the dichloride of copper as it forms. The dichloride of copper then acts upon another portion of the sulphide of silver, forming disulphide of copper and chloride of silver: $Cu^2Cl + AgS = Cu^2S + AgCl$. The chloride of silver thus produced, dissolves in the chloride of sodium, and is decomposed by the mercury subsequently

added, yielding calomel and metallic silver. This process is always attended with considerable loss of mercury, which however may be diminished by the previous addition of iron. Mr. P. Johnston proposes to diminish the loss of mercury, as soluble chloride, which occurs in this process, by using an amalgam of zinc and mercury, instead of pure mercury.

Silver is obtained free from other metals, and in a state of purity, for chemical and other purposes, by the following processes: — 1. The metal is dissolved in pure nitric acid slightly diluted, and precipitated by a solution of chloride of sodium, the salts of the other metals present remaining in solution. The insoluble chloride of silver, thus obtained, is thoroughly washed upon a filter with hot water and dried. A quantity of carbonate of potash, equal to twice the weight of the silver, is then fused in a crucible, and the chloride of silver gradually added to it, whereupon chloride of potassium is formed, and carbonic acid and oxygen escape with effervescence. The crucible is then exposed to a heat sufficient to fuse the reduced silver, which subsides to the bottom.—2. The mode of separating silver from the common metals, in the ordinary practice of assaying, is, like many metallurgic operations, an exceedingly elegant and refined process. A portion of the silver alloy, the *assay*, is fused with several times its weight of pure lead (an alloy of 1 copper and 15 silver with 96 lead, for instance) upon a bone-earth cupel, which is supported in a little oven or muffle, heated by a proper furnace. Air being allowed access to the assay, the lead is rapidly oxidated, and its highly fusible oxide imbibed, as it is produced, by the porous cupel. The disposition of copper and other common metals to oxidate is increased by the presence of the lead; and their oxides, which form fusible compounds with oxide of lead, are removed in company with the latter. When the foreign metal is almost entirely removed, the assay is observed to become rounder and more brilliant, and the last trace of fused oxide occasions a beautiful play of prismatic

colours upon its surface, after which the assay becomes, in an instant, much whiter, or *flashes*, an indication that the cupellation is completed.

Pure silver may also be obtained from an alloy containing only silver and copper, by precipitating the two metals with excess of carbonate of soda with the aid of heat, boiling the precipitate for about ten minutes with a solution of grape-sugar, whereby the copper is reduced to the state of red oxide, and the silver to the metallic state, and treating the moist precipitate with a hot solution of carbonate of ammonia: the copper then dissolves, and pure silver remains.

Pure silver is the whitest of the metals, and susceptible of the highest polish; when granulated by being poured from a height of a few feet into water, its surface is rough, but its aspect peculiarly beautiful. It crystallises in cubes and regular octohedrons, both from a state of fusion and by precipitation from solution. Silver is in the highest degree ductile and malleable; its density varies between 10·474 and 10·542; it fuses at 1873°. When in the liquid state, it is capable of absorbing oxygen gas from the air, which is discharged again in the solidification of the metal, and gives rise to a sort of vegetation upon its surface, or even occasions the projection of small portions of the silver to a distance, an accident which is known in assaying as the *spitting* of the metal. Gay-Lussac observed, that when a little nitre was thrown upon the surface of melted silver in a crucible, and the whole kept in a state of fusion for half an hour, a very considerable absorption of oxygen took place. When the crucible was removed from the fire and quickly placed under a bell-jar filled with water, which can be done without danger, the silver discharged a quantity of oxygen equal to 20 times its volume. This property is possessed only by pure silver, and does not appear at all in silver containing 1 or 2 per cent. of copper. As oxide of silver is reduced by a red heat, the absorption of the oxygen by the

fluid metal must be a phenomenon of a different nature from simple oxidation.

Silver does not combine with the oxygen of the air at the usual temperature, nor even when heated; the tarnishing of polished silver in air is occasioned by the formation of sulphide of silver. Silver does not dissolve in any hydrated acid, by substitution for hydrogen, but on the contrary is displaced from solution in an acid by hydrogen, and precipitated in the metallic state. This metal is also precipitated by mercury and by all the more oxidable metals. Its salts are reduced at the usual temperature by sulphate of iron, the protoxide in which is converted into sesquioxide. But if the ferric sulphate is boiled upon the precipitated silver, the latter is dissolved again, and oxide of silver and protoxide of iron reproduced. Silver, however, is oxidated when fused or heated strongly in contact with substances for which oxide of silver has a great affinity, as with a siliceous glass, and stains the glass yellow. It is oxidated by concentrated sulphuric acid, with evolution of sulphurous acid. Silver is readily dissolved by nitric acid, at a gentle heat, and with much violence, at a high temperature, nitrate of silver being formed, and nitric oxide escaping. Silver combines in three proportions with oxygen, forming a suboxide, Ag_2O, a protoxide AgO, and a peroxide, AgO_2.

Suboxide of silver, Ag_2O.—Pure protoxide of silver is completely reduced to the state of metal by hydrogen gas, at 212°; but the oxide contained in citrate of silver loses only half its oxygen under the same circumstances, the suboxide being formed and remaining in combination with one half of the citric acid of the former salt. The aqueous solution of the suboxide salt is dark brown, and the suboxide is precipitated black from it by potash. When the solution of the subsalt is heated, it becomes colourless, and metallic silver appears in it. The salt dissolves with a brown colour in ammonia. Several other salts of silver, containing organic

acids, comport themselves in the same way as the citrate, when heated in hydrogen.* A solution of protoxide of silver in ammonia deposits on exposure to the air, a grey suboxide, containing 108 parts of silver to 5·4 parts oxygen. When heated, it gives off oxygen and leaves metallic silver (Faraday).†

Protoxide of silver, AgO, 116 *or* 1450.—This oxide is thrown down, when potash or lime-water is added to a solution of nitrate of silver, as a brown powder, which becomes of a darker colour when dried. The powder was found to be anhydrous by Gay-Lussac and Thénard; its density is 7·143, according to J. Herapath; 7·250, according to P. Boullay; 8·2558, according to Karsten. Oxide of silver is decomposed by light, or at a red heat, into oxygen gas and metallic silver. Hydrogen reduces it even at 212°. It is also reduced by an aqueous solution of phosphorous acid. When recently precipitated, it is decomposed by aqueous sulphurous acid, yielding metallic silver and sulphate of silver; but the decomposition is only partial, even when aided by heat. When immersed in water, it is reduced by zinc, cadmium, tin, and copper, but not by iron or mercury. In an aqueous solution of hypochlorous acid, it is converted into chloride of silver, oxygen being evolved together with a small quantity of chlorine.

Oxide of silver is a powerful base, and forms salts, several of which have been found isomorphous with the corresponding salts of soda. Like oxide of lead, it dissolves to a small extent in pure water free from saline matter, and the solution has an alkaline reaction. Oxide of silver is not dissolved by solutions of the hydrates of potash and soda. Its salts are precipitated black by *hydrosulphuric* acid and *alkaline sulphides*. When treated with *hydrochloric* acid or a *soluble chloride*, they yield a white curdy precipitate, the chloride of silver, which soon becomes purple, if exposed, while moist, to

* Ann. Ch. Pharm. xxx. 1.

† Ann. Ch. Phys. [2], ix. 107.

the direct rays of the sun. This precipitate is not dissolved by nitric acid, but is dissolved by ammonia in common with most of the insoluble salts of silver. This precipitate is visible, according to Lassaigne, even in solutions containing only 1 part of silver in 800,000 parts of liquid. In a solution containing 1 part of silver in 200,000 parts, hydrochloric acid or common salt produces a slight turbidity; with 1 part of silver in 400,000, the same reagents produce a scarcely perceptible opalescence; and if the proportion of liquid amounts to 800,000 parts, the opalescence does not show itself for a quarter of an hour. *Hydrobromic acid* and soluble metallic *bromides*, added to solutions of silver salts, throw down all the silver in the form of yellowish white bromide, insoluble in nitric acid, and sparingly soluble in ammonia. *Hydriodic* acid and soluble *iodides* form a pale yellow precipitate of iodide of silver, likewise insoluble in nitric acid, and still less soluble in ammonia. *Hydrocyanic* acid and soluble *cyanides* throw down a white precipitate of cyanide of silver, easily soluble in ammonia, insoluble in cold dilute nitric acid, but dissolved by strong nitric acid at a boiling heat, with evolution of nitric oxide. *Ammonia* added in very small quantity to perfectly neutral silver-salts, produces a slight brown precipitate of oxide of silver, easily soluble in excess; but if the solution contains excess of acid, ammonia produces no precipitate. *Potash* added to the ammoniacal solution produces a white precipitate, provided the excess of ammonia be but small. The *fixed alkalies* form, in neutral or acid solutions of silver-salts, a brown precipitate of oxide of silver, insoluble in excess. *Alkaline carbonates* precipitate white carbonate of silver, soluble in ammonia and carbonate of ammonia. *Ordinary tribasic phosphate of soda* forms a yellow precipitate; *pyrophosphate* and *metaphosphate of soda* form white precipitates. *Chromate of potash* forms a dark crimson precipitate of chromate of silver. *Alkaline arsenites* form a canary-yellow precipitate of arsenite of silver. *Oxalic acid*

forms a white pulverulent precipitate of oxalate of silver. Silver is precipitated from its solutions in the metallic state by *phosphorus, phosphorous acid, phosphuretted hydrogen,* and *sulphurous acid* (imperfectly); by various *metals,* viz., zinc, cadmium, tin, lead, iron, manganese, copper, mercury, bismuth, tellurium, antimony, and arsenic; also by protoxide of uranium, hydrated protoxide of manganese, and protoxide of tin; and by various *organic substances* at a boiling heat, *e.g.,* charcoal, sugar, aldehyde, formic acid, tincture or infusion of galls, and volatile oils. Many organic substances added to a solution of nitrate of silver mixed with excess of ammonia, throw down metallic silver in the form of a beautiful specular film lining the sides of the vessel. This effect is produced by aldehyde, saccharic acid, salicylous acid, pyromeconic acid, and various essential oils. A mixture of oil of cinnamon and oil of cloves is found to produce an exceedingly brilliant speculum, and has indeed been used for silvering mirrors in place of the ordinary process with tin and mercury; it is particularly adapted for silvering curved surfaces. A very bright and regular specular surface is also produced by adding a solution of milk-sugar to an ammoniacal solution of nitrate of silver mixed with caustic potash or soda; the precipitation then takes place without the application of heat (Liebig).*

Oxide of silver combines with ammonia and forms the fulminating *ammoniuret of silver,* a substance of a dangerous character from the violence with which it explodes. The ammoniuret may be formed by digesting newly precipitated oxide of silver in strong ammonia, or more readily by dissolving nitrate of silver in ammonia, and precipitating the liquor by potash in slight excess. If this substance be pressed by a hard body, while still moist, it explodes with unequalled violence; when dry, the touch of a feather is often sufficient to cause it to fulminate. The explosion is obviously occa-

* Ann. Ph. Pharm. xcviii. 132.

sioned by the reduction of the silver from the combination of its oxygen with the hydrogen of the ammonia, and the evolution of nitrogen gas.

Sulphide of silver, AgS, 124 *or* 1550.—Sulphur and silver may be combined together by fusion; the excess of sulphur escapes, and at a high temperature the sulphide melts; it forms, on cooling, a crystalline mass. This compound has a lead-grey colour and metallic lustre. It is so soft that it may be cut with a knife, and is malleable. The sulphide of silver is also remarkable for conducting electricity, like a metal, when warmed. The same compound occurs in nature, sometimes crystallised in octohedrons with secondary faces. This sulphide is particularly interesting from being isomorphous with the subsulphide of copper, AgS with Cu_2S (page 144). These two sulphides replace each other in indeterminate proportions in several double sulphides of silver and other metals, as in *polybasite* and *fahl-ores*, the composition of which may be expressed by the following formulæ, the symbols placed above each other representing constituents, of which either the one or the other may be present:

$$\text{Polybasite} \quad . \quad 9\genfrac{}{}{0pt}{}{Cu_2S}{AgS} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}$$

$$\text{Fahl-ores} \quad \left(4\genfrac{}{}{0pt}{}{ZnS}{FeS} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}\right) + 2\left(4\genfrac{}{}{0pt}{}{AgS}{Cu_2S} + \genfrac{}{}{0pt}{}{SbS_3}{AsS_3}\right).$$

Chloride of silver, AgCl, 143·5 *or* 1793·75.—This salt contains in 100 parts, 24·69 parts of chlorine, and 75·31 parts of silver. It is found native as *horn-silver*, in translucent cubes or octohedrons of a greyish-white colour, and specific gravity 5·55. The same compound is also thrown down as a white precipitate, at first very bulky and curdy, when hydrochloric acid or a soluble chloride is added to any soluble salt of silver, except the hyposulphite. It is wholly insoluble in water, and the most minute quantity of hydrochloric acid contained in water may be detected by adding to

it a drop of a solution of nitrate of silver (p. 336.) Hydrochloric acid, when concentrated, dissolves chloride of silver, which crystallises from it in octohedrons, when the solution is evaporated. This salt dissolves easily in solution of ammonia, and crystallises also as the ammonia evaporates. When heated, it fuses at about 500°, forming a transparent yellowish liquid, which becomes, after cooling, a mass that may be cut with a knife, and has considerable resemblance to horn: a property to which it was indebted for the name of *horn-silver*, applied to it by the older chemists. It is not volatile. Chloride of silver is not affected by a concentrated solution of potash. It is easily reduced to the state of metal by zinc or iron with water. Chloride of silver may be dissolved out in this way by means of zinc and acidulated water, from a porcelain crucible in which it has been fused. To obtain pure silver by this mode of reduction, it is necessary to use zinc free from lead, otherwise that metal, not being dissolved by the sulphuric acid, remains mixed with the silver. A better mode of reduction is to boil the chloride of silver with an equal weight of starch-sugar and a solution of one part of carbonate of soda in three parts of water (Böttger). The chloride and other salts of silver acquire a dark colour when exposed to light; chlorine escapes, and a portion of the salt appears to be reduced to the metallic state, as the blackened surface conducts electricity. According to Wetzlar, the black substance contains an inferior chloride of silver, and is not attacked by nitric acid, or soluble in ammonia. It has also been supposed that the blackening is due, not to any chemical decomposition, but merely to a change in the state of aggregation of the particles. It appears, however, from some recent experiments by Dr. F. Guthrie, that the chloride is completely decomposed and metallic silver separated, even in presence of free nitric acid. Paper charged with chloride of silver is very sensitive to the impression of light, and is the material used for positive photographs, the unaltered chloride

being afterwards dissolved out by a solution of hyposulphite of soda.

One hundred parts of chloride of silver absorb 17·9 parts of ammoniacal gas, forming the compound, $3NH_3 . 2AgCl$, or $N \left. \begin{matrix} \overbrace{H(NH_4)_2Ag} \\ Ag \end{matrix} \right\} Cl_2$. This compound gives off its ammonia in the air. Chloride of silver is dissolved by concentrated and boiling solutions of the chlorides of potassium, sodium, and ammonium, and, on cooling, a double salt is deposited in crystals, generally cubes. Chloride of silver is also dissolved by cyanide of potassium, and the solution yields a double salt by evaporation (Liebig).

Bromide of silver, AgBr, 188 *or* 2350.—This salt consists in 100 parts, of 42·56 bromine and 57·44 silver. It is found native in Mexico and in Bretagne; sometimes in small amorphous masses, sometimes in greenish-yellow octohedral crystals. It is insoluble in water, and falls as a precipitate which is white at first, but becomes pale yellow when collected. When fused and cooled, it yields a mass of a pure and intense yellow colour. It has most of the properties of chloride of silver, but dissolves very sparingly in ammonia.

Iodide of silver, AgI, 234·36 *or* 2929·5.—This salt contains in 100 parts, 53·87 of iodine and 46·13 of silver. It is found native, sometimes in regular hexagonal prisms. It is insoluble in water, like the chloride, and is prepared in a similar manner by precipitation, but is distinguished from that salt by its colour, which is pale yellow, by the difficulty with which it is dissolved in ammonia, being even less soluble than the bromide, and by being blackened more slowly by the action of light. According to Martini, 2500 parts of ammonia, of density 0·960, are required to dissolve one part of iodide of silver. It is soluble to a large extent, at the boiling temperature, in concentrated solutions of the alkaline and earthy iodides, and forms with them double salts.

Silver is rapidly dissolved by hydriodic acid, with evolution

of hydrogen. If the action is assisted by heat, the solution deposits, on cooling, a colourless crystalline salt, resembling nitrate of silver, but decomposing as soon as it is separated from the liquid: it appears to consist of an iodide of silver and hydrogen. The mother-liquor, when left to itself, deposits iodide of silver in large regular six-sided prisms, resembling the native iodide (H. Ste.-Claire Deville).*

Fluoride of silver, AgF, is obtained by dissolving the oxide or carbonate in hydrofluoric acid. It is very soluble in water, and is partly decomposed by evaporation.

Cyanide of silver, AgCy; 134 *or* 1675.—This salt contains, in 100 parts, 19·41 cyanogen and 80·59 silver. It falls as a white powder when hydrocyanic acid is added to a solution of nitrate of silver. It is distinguished from chloride of silver by dissolving in concentrated nitric and sulphuric acids, when heated. It is readily decomposed by hydrochloric acid, and yields hydrocyanic acid, 100 parts of cyanide of silver giving 20·36 parts of hydrocyanic acid. It is decomposed by a red heat, giving off half its cyanogen and leaving paracyanide of silver, Ag_6Cy_3. Cyanide of silver is dissolved by cyanide of potassium, and other soluble cyanides. The double cyanide of potassium and silver crystallises in octohedrons, KCy . AgCy.

Carbonate of silver, $AgO.CO_2$, is a white insoluble powder.

Sulphate of silver, $AgO.SO_3$; 156 *or* 1950.—Obtained by dissolving silver, with heat, in concentrated sulphuric acid, or by precipitating a solution of nitrate of silver with sulphate of potash. It is soluble in 88 times its weight of boiling water, and crystallises, on cooling, in the form of anhydrous sulphate of soda. This salt is highly soluble in ammonia, and gives, by evaporation, an ammoniacal sulphate of silver in fine transparent crystals, which are persistent in air; $AgO.SO_3 + 2NH_3$, or $\overbrace{NH_2(NH_4)Ag}.SO_4$. Chromate and

* Compt. rend. xlii. 894.

seleniate of silver form analogous compounds with ammonia, which are all isomorphous. The bichromate of silver is also isomorphous with bichromate of soda.

Hyposulphate of silver, $AgO.S_2O_5$, is soluble in water, and crystallises in the same form as hyposulphate of soda. It crystallises also with ammonia, as $AgO.S_2O_5 + 2NH_3$, or $N\,\overbrace{H_2(NH_4)Ag}.S_2O_6$.

Hyposulphite of silver, $AgO.S_2O_2$.— Hyposulphurous acid appears to have a greater affinity for oxide of silver than for any other base. Oxide of silver decomposes the alkaline hyposulphites, liberating one-half of their alkali, and forming a double hyposulphite of the alkali and silver. These double salts are best prepared by adding chloride of silver in small portions to the soluble hyposulphite of potash, soda, ammonia, or lime in the cold, till the liquid is saturated; after which, the solution is filtered, and mixed with a large quantity of alcohol, which precipitates the double salt; the potash and soda salts are crystallisable. Herschel considers the double salts obtained in this manner as probably containing one eq. of hyposulphite of silver to two eq. of the other hyposulphite. The solution of one of these double salts dissolves more oxide of silver, and forms a double salt, which is believed to contain single equivalents of the salts, and precipitates as a white crystalline, pulverulent, bulky mass. The second compound is sparingly soluble in water, but dissolves in ammonia, and communicates to the liquor an intensely sweet taste.

The hyposulphite of silver itself is an insoluble substance; it is prone to undergo decomposition, changing spontaneously into sulphate and sulphide of silver. When to a dilute solution of nitrate of silver, a dilute solution of hyposulphite of soda is added by small quantities, a white precipitate of hyposulphite of silver falls, which dissolves again in a few seconds, from the formation of the soluble double hyposulphite of soda and silver. When enough of hyposulphite of soda has been

gradually added to render the precipitate permanent, without, however, decomposing the whole silver salt, a flocculent mass is obtained of a dull grey colour, which is permanent. The liquor contains much hyposulphite of silver, and has an intensely sweet taste, not at all metallic; the silver is not precipitated from it by hydrochloric acid or the chlorides. An excess of hyposulphite of soda destroys the precipitated hyposulphite of silver, converting it into sulphide of silver.

Nitrate of silver, $AgO \cdot NO_5$; 170 *or* 2125.—When a piece of pure silver is suspended in nitric acid, it dissolves for a time without effervescence at a low temperature, nitrous acid being produced, which colours the liquid blue; but if heat be applied or the temperature allowed to rise, then the metal dissolves with violent effervescence, from the escape of nitric oxide. The nitrate of silver crystallises on cooling in colourless tables, which are anhydrous. It is soluble in 1 part of cold, in ½ part of hot water, and in 4 parts of boiling alcohol. The solution of this salt does not redden litmus paper, like most metallic salts, but is exactly neutral. Nitrate of silver fuses at 426°, and forms a crystalline mass on cooling; it is cast into little cylinders for the use of surgeons. It is sometimes adulterated in this state with nitrate of potash, which may be detected by the alkaline residue which the salt then leaves when heated before the blowpipe, — or with nitrate of lead, in which case the solution of the salt is precipitated by iodide of potassium, of a full yellow colour. When applied to the flesh of animals, it instantly destroys the organisation and vitality of the part. It forms insoluble compounds with many kinds of animal matter, and is employed to remove it from solution. When organic substances, to which a solution of nitrate of silver has been applied, are exposed to light, they become black from the reduction of the oxide of silver to the metallic state. A solution of nitrate of silver in ether is employed to dye the hair black. One part of nitrate of silver and 4 parts of gum arabic dissolved in 4 parts of water, and

blackened with a small quantity of Indian ink, form the indelible marking ink used to write upon linen. The part of the linen to be marked should be first wetted with a solution of carbonate of soda and dried, and the writing should be exposed to the light of the sun. For this ink, which is expensive, another liquid has been substituted by bleachers, namely coal tar, made sufficiently thin with naphtha to write with, which is found to resist chlorine, and to answer well as a marking ink.

A strong solution of nitrate of silver absorbs two equivalents of ammoniacal gas, and forms the crystallisable *Ammoniacal nitrate of silver*, $AgO \cdot NO_5 + 2NH_3 = N\,\overbrace{H_2(NH_4)Ag} \cdot NO_6$. The dry nitrate in powder absorbs three atoms of ammonia, $AgO.NO_5 + 3NH_3 = N\,\overbrace{H(NH_4)_2Ag} \cdot NO_6$.

Nitrate of silver forms a double salt with nitrate of the red oxide of mercury, which crystallises in prisms. Nitrate of silver and cyanide of mercury also form a double salt, when hot solutions of them are mixed: $AgO.NO_5 + 2HgCy + 8HO$. Cyanide of silver is soluble in a boiling solution of nitrate of silver, and forms a crystalline compound, $AgO.NO_5 + 2AgCy$, which is decomposed by water.

Nitrite of silver, $AgO \cdot NO_3$; 154 or 1925. — Nitrate of soda is fused at a red heat, till it is wholly converted into nitrite by loss of oxygen; the latter salt then begins to give off nitrous acid, and a small portion of the salt dissolved in water will be found to precipitate silver brown. The fusion is then interrupted, the salt dissolved in boiling water, precipitated by nitrate of silver, and filtered while still very hot. The nitrite of silver, which requires 120 times its weight of water at 60° to dissolve it, is precipitated as the solution cools. The other nitrites are prepared by rubbing this salt in a mortar with chlorides taken in equivalent quantities. It appears from experiments of Proust, that two subnitrites of silver exist, one soluble and the other insoluble.

Acetate of silver, which is soluble in 100 times its weight

of cold water, is precipitated when acetate of copper is mixed with a concentrated solution of nitrate of silver. It crystallises from solution in boiling water in anhydrous needles.

Oxalate of silver is an insoluble powder. A double *oxalate of potash and silver* is formed by saturating binoxalate of potash with carbonate of silver. It is very soluble, and forms rhomboidal crystals, which are persistent in air.

Peroxide of silver.—A superior oxide of silver is deposited upon the positive pole or zincoid of a voltaic battery in a weak solution of nitrate of silver, in the form of needles of 3 or 4 lines in length, which are black and have a metallic lustre, while metallic silver is, at the same time, deposited in crystals upon the negative pole or chloroid. The former crystals are converted by sulphuric acid into oxide of silver and oxygen, and yield with hydrochloric acid, chloride of silver and chlorine. According to Fischer, whose observations are confirmed by L. Gmelin, the peroxide prepared as above from nitrate of silver always retains nitric acid, and if prepared in a similar manner from the sulphate, it always retains sulphuric acid.*

Alloys of silver.—Silver may be readily alloyed with most metals. It combines by fusion with iron, from which it cannot be separated by cupellation. Native silver is always associated with gold; the two metals are found crystallised together in all proportions in the same cubic or octohedral crystals. Gold may be detected in a silver coin, by dissolving the latter in pure nitric acid, when a small quantity of black powder remains, which after being washed with water, will be found to dissolve in nitro-hydrochloric acid, giving a yellow solution, in which protochloride of tin produces a precipitate of the purple powder of Cassius. Pure silver, being very soft, is always alloyed in coin and plate, with a certain

* Gmelin's Handbook, Translation, vi. 145.

quantity of copper, to make it harder. The standard silver of England is an alloy of 222 pennyweights of silver with 18 pennyweights of copper., or it contains 92·5 per cent. of silver. The standard of the Spanish dollar, of the French and most other coinages, is 90 per cent. of silver. The alloy of silver and copper of greatest stability consists of 71·9 silver, and 28·1 copper, and corresponds with the formula $AgCu_4$.*

ESTIMATION OF SILVER, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Silver, when in the state of solution, is always estimated as chloride. The solution, if not already acid, is slightly acidulated with nitric acid; the silver precipitated with hydrochloric acid, and the liquid placed for some hours in a warm situation to cause the precipitated chloride of silver to settle down. The precipitate is collected on a filter, which should be as small as possible, washed with water, and dried at 212°. It must then be separated as completely as possible from the filter; introduced into a porcelain crucible, previously weighed; the filter burnt to ashes outside the crucible; the ashes added to the contents of the crucible; and the whole strongly heated over a lamp till the chloride of silver is brought to a state of tranquil fusion, after which it is left to cool and weighed. It contains 75·26 per cent. of silver. This mode of estimation is affected with an error, arising from the partial reduction of the chloride of silver by the organic matter of the filter. The error thus occasioned is but slight when the process is well conducted, and may always be obviated by treating the fused chloride after cooling with nitric acid to dissolve the reduced silver; then adding hydrochloric acid, evaporating to dryness, and again fusing the residue. Another mode of proceeding is to collect the chloride of silver on a weighed filter, and dry it in an oil-

* Levol, Ann. Ch. Phys. [3], xxxvi. 220.

bath, at about 300° F. The chloride may also be washed by decantation, and the use of a filter avoided altogether; but the washing requires very careful manipulation.

The quantity of silver in a solution may also be determined by precipitating it with a solution of chloride of sodium of known strength. The solution of chloride of sodium is made of such a strength that a cubic decimetre of it exactly precipitates 1 gramme of pure silver. It is added to the silver solution from a burette, divided into cubic centimetres, the liquid being well shaken after each addition, to cause the precipitate to settle down. The number of cubic centimetres of solution thus added determines the quantity of silver present.

As silver is reduced from many of its salts by the mere action of heat, the quantity of silver in such compounds may be readily determined by simply igniting them in a porcelain crucible. This method is applicable to nearly all salts of silver which contain organic acids. It must be observed, however, that in some cases, a certain quantity of carbon remains combined with the silver, and that some organic silver compounds containing nitrogen leave cyanide of silver when ignited.

The method of precipitating by hydrochloric acid serves to separate silver from all other metals. If lead be present in solution with silver, the liquid must be diluted with a large quantity of water before the hydrochloric acid is added; because the chloride of lead is but sparingly soluble. The separation of silver from lead may also be effected by precipitating both the metals as chlorides, and dissolving the chloride of silver in ammonia. To separate silver from mercury, the latter metal, if in the state of mercurous oxide, must first be converted into mercuric oxide by oxidation with nitric acid.

The estimation of the quantity of silver in alloys, such as coins, is usually effected either by cupellation in the manner

already described (p. 332.), or by dissolving the alloy in nitric acid, and precipitating the silver with a graduated solution of chloride of sodium.*

The cupellation of silver is always attended with a certain loss, arising partly from a portion of the melted silver being absorbed by the cupel, and partly by volatilisation. The loss thus occasioned varies with the proportion of lead employed in the cupellation, with the proportion of silver in the alloy, and likewise with the heat of the furnace: hence the results obtained require a certain correction, the amount of which must be determined by special trials made upon alloys of known composition and with different proportions of lead.

SECTION III.

GOLD.

Eq. 98·33 *or* 1229·16; Au. (*Aurum.*)

Gold is found in small quantity in most countries, sometimes mixed with iron pyrites, copper pyrites, and galena, but generally native, massive, and disseminated in threads through crystalline rocks, such as quartz, or in grains among the sand of rivers, and in alluvial deposits formed by the disintegration of ancient rocks. In these deposits, some of which are of great extent, gold is occasionally found in masses of considerable size, called *nuggets*. Formerly, the principal supply of this metal was from the mines of South America, Hungary, and the Uralian mountains; but of late years, the largest quantities have been obtained from California and Australia. Native gold is sometimes pure, but is more frequently associated in various proportions with silver.

* The process, by Guy-Lussac, for this purpose is described, with the requisite Tables, in the Parliamentary Report upon the Royal Mint, 1837, Appendix, p. 145. See also *Dr. Miller's Elements of Chemistry*, p. 1035.

Gold is separated from the substances with which it is mechanically associated, either by washing with water, whereby the earthy matters are carried away while the heavy gold particles remain behind, or by amalgamation. The small quantity of gold which occurs, generally associated with silver, in certain lead and copper ores, is extracted by liquation and cupellation, in the manner already described for silver. By these processes, gold is obtained free from all other metals except silver, and from this it may be separated by nitric acid, which dissolves the silver, but only when it forms a large proportion of the alloy. When nitric acid does not dissolve the silver, the alloy is submitted to an operation termed *quartation*, which consists in fusing it with four times its weight of silver, after which the whole of the silver may be dissolved out by nitric acid.

Pure gold may be obtained from any alloy containing it, by dissolving the alloy in a mixture of two measures of hydrochloric and one measure of nitric acid; separating the solution from insoluble chloride of silver by filtration; evaporating it over the water-bath till acid vapours cease to be exhaled; then dissolving the residue in water acidulated with hydrochloric acid; and adding protosulphate of iron, which completely precipitates the gold in the form of a brown or brownish-yellow powder, the protosulphate of iron being at the same time converted into sesquisulphate and sesquichloride:

$$6(FeO \cdot SO_3) + Au_2Cl_3 = 2(Fe_2O_3 \cdot 3SO_3) + Fe_2Cl_3 + 2Au.$$

The gold thus precipitated is quite destitute of metallic lustre, but acquires that character by burnishing.

From alloys of gold and silver, or of gold, silver, and copper, the gold may also be separated by the action of strong sulphuric acid. The alloy, after being granulated by pouring it in the melted state into water, is heated in a platinum or cast-iron vessel with $2\frac{1}{2}$ times its weight of sulphuric acid

of specific gravity 1·815 (66° Baumé), the heat being continued as long as sulphurous acid is evolved. The silver and copper are thereby converted into sulphates, while the gold remains unattacked. The solution is boiled for a quarter of an hour with an additional quantity of sulphuric acid of specific gravity 1·653, or 58° Baumé (obtained by concentrating the acid mother-liquors of sulphate of copper produced in the operation), and afterwards left at rest. The gold then settles down, and the liquid, after being diluted with water, is transferred to a leaden vessel and again boiled with sheets of copper immersed in it. The silver is then precipitated in the metallic state, while the copper is converted into sulphate, and dissolves. The gold deposited in the manner above described still retains a small quantity of silver, from which it is separated by treating it a second and a third time with strong sulphuric acid: it then retains only 0·005 of silver. This process is not applicable to alloys containing more than 20 per cent. of gold; richer alloys must first be fused with the requisite quantity of silver. It is applied on the large scale to the extraction of gold, chiefly from alloys which contain but little of that metal, such as native silver and old silver coins, and, as now practised, is economically available even when the amount of gold does not exceed one part in 2000.

Gold is the only metal of a yellow colour. When pure, it is more malleable than any other metal, and nearly as soft as lead. Its ductility appears to have scarcely a limit. A single grain of gold has been drawn into a wire 500 feet in length, and this metal is beaten out into leaves which have not more than 1-200,000th of an inch of thickness. The coating of gold on gilt silver wire is still thinner. Gold, when very thin, is transparent, thin gold leaf appearing green by transmitted light. The green colour passes into a ruby red when highly attenuated gold is heated: in the red gold-glass, the gold is in the metallic state (Faraday). The point of fusion of this

metal is 2192°, according to Pouillet; 2518°, according to Guyton-Morveau; and 2590°, according to Daniell: it contracts considerably upon becoming solid. The density of gold varies from 19·258 to 19·367, according as it has been more or less compressed. Gold does not oxidate or tarnish in air, at the usual temperature, nor when strongly ignited. But this and the other noble metals are dissipated and partly oxidated, when a powerful electric charge is sent through them in thin leaves. It is not dissolved by nitric, hydrochloric, or sulphuric acid, or indeed by any single acid. It is acted upon by chlorine, which converts it into sesquichloride, and by acid-mixtures, such as aqua-regia, which evolve chlorine. It combines in two proportions with oxygen, forming the two oxides Au_2O and Au_2O_3, which show but little tendency to combine with acids. Some chemists, however, double the atomic weight of gold, and regard these oxides as protoxide, AuO, and teroxide, AuO_3, respectively.

Oxide of gold, Aurous oxide, Au_2O, 204·66 or 2558·25.— This oxide is obtained as a green powder by decomposing the corresponding chloride of gold with a cold solution of potash. It is partly dissolved by the alkali, and soon begins to undergo decomposition, being resolved into the higher oxide and metallic gold. The latter forms upon the sides of the vessel a thin film, which is green by transmitted light, like gold leaf.

Chloride of gold, Aurous chloride, Au_2Cl, is obtained by evaporating a solution of the sesquichloride to dryness, and heating the powder thus obtained in a sand-bath, retaining it at about the temperature of melting tin, and constantly stirring it, so long as chlorine is evolved. It is a white, saline mass, having a tinge of yellow, and quite insoluble in water. In the dry state it is permanent, but in contact with water it gradually undergoes decomposition, and is converted into gold and the sesquichloride. This change takes place almost instantaneously at the boiling temperature.

Aurous iodide, Au_2I, is formed by the action of hydriodic acid on auric oxide, water being formed and two-thirds of the iodine set free:

$$Au_2O_3 + 3HI = Au_2I + 3HO + 2I;$$

also by adding iodide of potassium in proper proportion, and in successive small quantities, to an aqueous solution of auric chloride:

$$Au_2Cl_3 + 3KI = Au_2I + 3KCl + 2I.$$

It is a lemon-yellow, crystalline powder, insoluble in cold water, and very sparingly soluble in boiling water.

Aurous sulphide is formed when hydrosulphuric acid gas is passed into a boiling solution of the sesquichloride of gold. It is dark-brown, almost black. Aurous sulphide combines with the protosulphides of potassium and sodium, forming double salts containing 1 eq. of aurous sulphide with 1 eq. of the alkaline sulphide. The sodium-salt is obtained by fusing together 2 eq. protosulphide of sodium, 1 eq. gold, and 6 eq. sulphur; digesting the fused mass in water; filtering the yellow solution in an atmosphere of nitrogen; and concentrating in vacuo over sulphuric acid. Yellow crystals are then obtained, having the form of oblique hexagonal prisms with trilateral or quadrilateral summits, and containing $NaS . Au^2S + 8Aq$. They are soluble in water and alcohol. The potassium-salt, which is obtained in a similar manner, forms indistinct crystals (Col. Yorke).*

Sesquioxide of gold, Auric oxide, Au_2O_3, 220·66 *or* 2758·25. — This oxide has many of the properties of an acid. It is obtained by digesting magnesia in a solution of sesquichloride of gold, when an insoluble compound of auric oxide and magnesia is formed, which is collected upon a filter and well washed. The compound is afterwards digested in nitric acid, which dissolves the magnesia, with traces of auric oxide, but

* Chem. Soc. Qu. J. i. 236.

leaves the greater part of the latter undissolved. It is left in the state of a reddish-yellow hydrate, which when dried in air becomes chestnut-brown. When precipitated by an alkali, auric oxide carries down a portion of the latter, of which it may be deprived by nitric acid. Dried at 212°, it abandons its water, becomes black, and is in part reduced. When exposed to light, particularly to the direct rays of the sun, its reduction is very rapid. It is decomposed by an incipient red heat. Hydrochloric acid is the only acid which dissolves and retains this oxide, and then sesquichloride of gold is formed. It is dissolved by concentrated nitric and sulphuric acid, but precipitated from these solutions by water. The affinity of this oxide for alkaline oxides, on the contrary, is so great that, when boiled in a solution of chloride of potassium, it is dissolved, the liquid becoming alkaline, and *aurate of potash*, or a compound of auric oxide and potash, being formed. The compounds of auric oxide with the alkalies and alkaline oxides are nearly colourless, and are not decomposed by water. They appear to be of two different degrees of saturation, aurates which are soluble, and superaurates which are insoluble. The only one of these compounds which has been studied in some degree is the aurate of ammonia, or *fulminating gold* as it is named, from its violently explosive character.

Aurate of ammonia.—When the solution of gold is precipitated by a small quantity of ammonia, a powder of a deep yellow colour is obtained, which is a compound of aurate of ammonia with a portion of sesquichloride of gold. This compound explodes by heat, but the detonation is not strong. But when the solution of gold is treated with an excess of ammonia, and the precipitate well washed by ebullition in a solution of ammonia, or better in water containing potash, the fulminating gold has a yellowish brown colour with a tinge of purple. When dry, it explodes very easily with a loud report, accompanied by a feeble flame. It may be ex-

ploded by a heat a little above the boiling point of water, or by the blow of a hammer. Its composition has not been exactly determined; but if the ammonia is present in double the proportion that would contain the hydrogen necessary to burn the oxygen of the auric oxide, which Berzelius considers probable, its constituents may be $Au_2O_3 . 2NH_3 + HO$. The affinity of auric oxide for ammonia is so great, that it takes that alkali from all acids. Thus, when auric oxide is digested in sulphate of ammonia, fulminating gold is formed, and the liquid becomes acid.

Aurate of potash, $KO . Au_2O_3 + 6HO$.—Obtained in the crystalline state by evaporating a solution of sesquioxide of gold in a slight excess of pure potash, first over the open fire and afterwards in vacuo: the crystals may be freed from adhering potash by recrystallisation from water, then drained on unglazed porcelain and dried in vacuo. Aurate of potash is very soluble in water, and forms a yellowish strongly alkaline solution, which is decomposed by nearly all organic bodies, the gold being precipitated in the metallic state: it is also decomposed by heat. With most metallic salts it forms precipitates of aurates, which are insoluble in water, but soluble in excess of the precipitant; thus, chloride of calcium forms a precipitate of aurate of lime, soluble in excess of chloride of calcium. The solution of aurate of potash may be used as a bath for electro-gilding.

Aurosulphite of potash, $KO . Au_2O_3 + 4(KO . 2SO_2) + 5HO$; or $5KO\left\{\begin{matrix}Au_2O_3\\8SO_2\end{matrix}\right. + 5HO$. — Deposited in beautiful yellow needles when sulphite of potash is added drop by drop to an alkaline solution of aurate of potash. It is nearly insoluble in alkaline solutions, but dissolves with decomposition in pure water, especially if hot, giving off sulphurous acid and depositing metallic gold. Acids decompose it in a similar manner. After drying in vacuo, it may be preserved for two or three months, in well-closed bottles, but ultimately decom-

poses, giving off sulphurous acid and leaving metallic gold and sulphate of potash. The same decomposition takes place more quickly when the salt is heated (Fremy).*

Purple of Cassius.—When protochloride of tin is added to a dilute solution of gold, a purple-coloured powder falls, which has received that name. It is obtained of a finer tint when protochloride of tin is added to a solution of the sesquichloride of iron, till the colour of the liquid takes a shade of green, and the liquid in that state added, drop by drop, to a solution of sesquichloride of gold free from nitric acid, and very dilute. After 24 hours, a brown powder is deposited, which is slightly transparent and purple-red by transmitted light. When dried and rubbed to powder, it is of a dull blue colour. Heated to redness, it loses a little water, but no oxygen, and retains its former appearance. If washed with ammonia on the filter while still moist, it is dissolved, and a purple liquid passes through, which rivals the hypermanganate of potash in beauty. From this liquid, the colouring matter separates very gradually, weeks elapsing before the upper strata of the liquid become colourless; but it is precipitated more rapidly when heated in a close vessel between 140° and 180°. The powder of Cassius is insoluble in solutions of potash and soda. It may also be formed by fusing together 2 parts of gold, 3½ parts of tin, and 15 parts of silver, under borax, to prevent the oxidation of the tin, and treating the alloy with nitric acid to dissolve out the silver; a purple residue is left containing the tin and gold that were employed.

The powder of Cassius is certainly, after ignition, a mixture of binoxide of tin and metallic gold, from which the gold can be dissolved out by aqua-regia, while the binoxide of tin is left; and the last mode of preparing it, favours the idea that its constitution is the same before ignition; but the solubility of the unignited powder in ammonia, and the fact that mercury does not dissolve out gold from the powder when properly

* Ann. Ch. Pharm. lvi. 315.

prepared, appear to be conclusive against that opinion. The proportions of its constituents vary so much, that there must be more than one compound; or more likely the colouring compound combines with more than one proportion of binoxide of tin. Berzelius proposed the theory that the powder of Cassius may contain the true protoxide of gold combined with sesquioxide of tin, $AuO . Sn_2O_3$, a kind of combination containing an association of three atoms of metal, which is exemplified in black oxide of iron, spinell, gahnite, franklinite, and other minerals, and which we have repeatedly observed to be usually attended with great stability. A glance at its formula shows how readily the powder of Cassius, as thus represented, may pass into gold and binoxide of tin; $AuO . Sn_2O_3 = Au + 2SnO_2$. The existence of a purple oxide of gold, AuO, is not established; but it is probably the substance formed when a solution of gold is applied to the skin or nails, and which dyes them purple. Paper, coloured purple by a solution of gold, becomes gilt when placed in the moist state in phosphuretted hydrogen gas, which reduces the gold to the metallic state.

Pelletier gives the following method of preparing a purple of Cassius of constant composition: — 20 grammes of gold are dissolved in 100 grammes of aqua-regia containing 20 parts nitric to 80 parts of commercial hydrochloric acid; the solution is evaporated to dryness over the water-bath; the residue dissolved in water; the filtered solution diluted with 7 or 8 decilitres of water; and tin filings introduced into it: in a few minutes the liquid becomes brown and turbid, and deposits a purple precipitate, which merely requires to be washed and dried at a gentle heat. The purple thus prepared contains in 100 parts: 32·746 stannic acid, 14·618 protoxide of tin, 44·772 aurous oxide (Au_2O) and 7·864 water. The precipitate obtained by treating sesquichloride of gold with pure protochloride of tin is always brown. To obtain a fine purple precipitate, the chloride of gold should be treated with

a mixture of protochloride and bichloride of tin. The following process gives a fine purple:—*a.* A neutral solution is prepared of 1 part of tin in hydrochloric acid; *b.* A solution of 2 parts tin in cold aqua-regia (1 part hydrochloric acid to 3 nitric), the liquid being merely heated towards the end of the process, that it may not contain any protoxide of tin; *c.* Seven parts of gold are dissolved in aqua-regia (6 hydrochloric to 1 nitric), and the solution, which is nearly neutral, diluted with 3500 parts of water. To this solution *c*, the solution *b* is first added, and then the solution *a*, drop by drop, till the proper colour is produced. If the quantity of *a* be too small, the precipitate is violet; if too large, it is brown. It must be washed quickly, so that the liquid may not act upon it too long. It weighs 6½ parts (Bouisson).*

Sesquisulphide of gold, Au_2S_3, or *Auric sulphide*, is formed when a dilute solution of gold is precipitated cold by hydrosulphuric acid. It is a flocculent matter of a strong yellow colour, which becomes deeper by drying; it loses its sulphur at a moderate heat.

Sesquichloride of gold, Perchloride of gold, Auric chloride, Au_2Cl_3, 303·16 or 3789·5. — This compound is formed when gold is dissolved in aqua-regia. The solution is yellow, and becomes paler with an excess of acid, but is of a deep red when neutral in composition. It is obtained in the last condition by evaporating the solution of gold, till the liquid is of a dark ruby colour, and begins to emit chlorine. It forms on cooling a dark red crystalline mass, which deliquesces quickly in air. But the only method of procuring auric chloride perfectly free from acid salt, is to decompose aurous chloride with water. A compound of chloride of gold and hydrochloric acid crystallises easily from an acid solution, in long needles of a pale yellow colour, which are permanent in dry air, but run into a liquid in damp air. The solution of this salt deposits gold on its surface, and

* J. Pharm. [2], xvi. 629.

on the side of the vessel turned to the light. The gold is also precipitated in the metallic state by phosphorus, by most metals, by ferrous salts, by arsenious and antimonious acids, and by many vegetable and animal substances, by vegetable acids, by oxalate of potash, &c., carbonic acid then escaping. Hydrosulphuric acid and sulphide of ammonium throw down black sulphide of gold, soluble in excess of the latter re-agent. Ammonia and carbonate of ammonia produce a yellow precipitate of fulminating gold. Potash added in excess forms no precipitate, unless it contains organic matter, in which case a slight precipitate of aurous oxide is produced. Cyanide of potassium produces a yellow precipitate soluble in excess. Tincture of galls throws down metallic gold. Chloride of gold is soluble in ether and in some essential oils. It forms double salts with most other chlorides, which are almost all orange-coloured when crystallised; in efflorescing, they acquire a lemon-yellow colour, but in the anhydrous state they are of an intense red. They are obtained by evaporating the mixed solutions of the two salts.

Chloride of gold and potassium, $KCl . Au_2Cl_3 + 5HO$.— Crystallises in striated prisms with right summits, or in thin hexagonal tables which are very efflorescent; becomes anhydrous at 212°. The anhydrous salt fuses readily when heated, but loses chlorine and becomes a liquid, which is black while hot, and yellow when cold. It is then a compound of aurous chloride with chloride of potassium. *Chloride of gold and ammonium* crystallises in transparent prismatic needles, which become opaque in air; Mr. Johnston found their composition to be $NH_4Cl . Au_2Cl_3 + 2HO$. *Chloride of gold and sodium* crystallises in long four-sided prisms, and is persistent in air. Its composition is $NaCl . Au_2Cl_3 + 4HO$. Bonsdorff has prepared similar double salts with the chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. The salt of lime contains six, and the salt of magnesia twelve equivalents of water.

Sesquibromide of gold, Au_2Br_3, is formed by dissolving gold in a mixture of nitric and hydrobromic acids. It greatly resembles the sesquichloride, and forms also an extensive series of double salts.

Auric iodide, Au_2I_3, is formed by gradually adding a neutral solution of auric chloride to a solution of iodide of potassium: the liquid then acquires a dark-green colour, and yields a dark-green precipitate of Au_2I_3, which redissolves on agitation; but after 1 eq. of the auric chloride has been added to 4 eqs. of iodide of potassium, a further addition of the gold-solution decolorizes the liquid and forms a permanent precipitate of auric iodide, because the iodide of gold and potassium at first produced is thereby decomposed. The successive actions are represented by the following equations: —

$$(1.) \qquad 4KI + Au_2Cl_3 = 3KCl + KI \, . \, Au_2I_3 ;$$

$$(2.) \qquad 3(KI \, . \, Au_2I_3) + Au_2Cl_3 = 3KCl + 4Au_2I_3 .$$

Auric iodide is a very unstable compound; when exposed to the air at ordinary temperatures, it is gradually converted into yellow aurous iodide, and afterwards into metallic gold. It combines with hydriodic acid and with the more basic metallic iodides, forming a series of very dark-coloured salts; e. g. *iodo-aurate of potassium,* $KI \, . \, Au_2I_3$.

The oxides of gold show but little tendency to combine with oxygen-acids: the sesquioxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution.

Hyposulphite of aurous oxide and soda:

$$Au_2O \, . \, S_2O_2 + 3(NaO \, . \, S_2O_2) + 4HO ; \text{ or } \left.\begin{matrix} Au_2O \\ 3NaO \end{matrix}\right\} 4S_2O_2 + 4HO.$$

This salt is prepared by mixing concentrated solutions of sesquichloride of gold and hyposulphite of soda, and preci-

pitating with alcohol. When purified by repeated solution in water and precipitation by alcohol, it forms delicate, colourless needles. It has a sweetish taste, dissolves very easily in water, but very sparingly in alcohol. It is decomposed by heat and by nitric acid, with deposition of metallic gold. Its solution gives a blackish precipitate with hydrosulphuric acid and soluble sulphides. The presence of gold in this solution is not indicated by protosulphate of iron, protochloride of tin, or oxalic acid; and, on the other hand, sulphuric acid, hydrochloric acid, and the vegetable acids neither precipitate sulphur nor expel sulphurous acid from it. When mixed with chloride of barium, it yields a gelatinous precipitate of *Hyposulphite of aurous oxide and baryta*, containing $\left.\begin{matrix} Au_2O \\ 3BaO \end{matrix}\right\} 4S_2O_2$. Sulphuric acid removes all the baryta from this salt, and leaves *hydrated aurous hyposulphite*, which is uncrystallisable, strongly acid, and tolerably stable at ordinary temperatures. The solution of the soda-salt is used for fixing daguerreotype pictures (Fordos and Gélis).*

A *hyposulphite of auric oxide and soda* appears also to be formed by dropping a neutral solution of chloride of gold into aqueous hyposulphite of soda (Fordos and Gélis).

Alloys of gold.—Gold unites with nearly all metals; but its most important alloys are those which it forms with silver and copper. Gold which is used for coins, watches, articles of jewellery, &c., is always alloyed with copper, to increase its hardness, pure gold being much too soft for any of these purposes. The standard for coin in the United Kingdom is 11 gold with 1 alloy; in France and the United States of America, 9 gold to 1 alloy. For articles of jewellery, gold is also frequently alloyed with silver, which gives it a lighter colour. The alloys of gold, both with silver and with copper, are more fusible than gold itself. The solder used for gold

* Ann. Ch Phys. [3], xiii. 394.

trinkets is composed of 5 parts gold and 1 part copper, or of 4 parts gold, 1 part copper, and 1 part silver.

Amalgam of gold.—Gold unites readily with mercury, forming a white amalgam; the smallest quantity of mercurial vapour coming in contact with gold is sufficient to turn it white. Mercury is capable of dissolving a large quantity of gold without losing its fluidity, but, when quite saturated, it acquires a waxy consistence. When the liquid amalgam is strained through chamois-leather, mercury passes through together with a very small quantity of gold, and there remains a white amalgam, of pasty consistence, containing about 2 parts of gold to 1 part of mercury. By dissolving 1 part of gold in 1000 parts of mercury, pressing through chamois-leather, and treating the residue with dilute nitric acid at a moderate heat, a solid amalgam, Au_8Hg, is obtained, which crystallises in shining four-sided prisms, retains its lustre in the air, is not decomposed by boiling nitric acid, and does not melt even when heated till the mercury volatilises (T. H. Henry).*

Gilding and silvering.—The pasty amalgam of 2 parts gold and 1 part mercury is used for gilding ornamental articles of copper and bronze. The surface of the object is first thoroughly cleaned by heating it to redness, then plunging it into dilute sulphuric acid, and sometimes for an instant also into strong nitric acid; it is then *amalgamated* by washing it with a solution of nitrate of mercury, and afterwards pressed upon the pasty amalgam, a portion of which adheres to it. The mercury is then expelled by heat, and the gold-surface finally polished. Silver may be gilt by similar processes.

By substituting an amalgam of silver for the amalgam of gold, articles of copper, bronze, and brass may be *silvered* or *plated.*

Articles of copper, chiefly copper trinkets, are also gilt by

* Phil. Mag. [4], ix. 468.

immersion in a boiling solution of chloride of gold in an alkaline carbonate, after having been cleaned by processes similar to those just described.

But the process now most generally adopted is that of *electro-gilding,* which is performed by immersing the objects to be gilt in a solution of 10 parts of cyanide of potassium and 1 part of cyanide of gold in 100 parts of distilled water, and connecting them with the negative pole of a voltaic battery, while the positive pole is connected with a bar of gold also immersed in the liquid. The solution is then decomposed by the current, the gold being deposited on the objects at the negative pole, while the gold connected with the positive pole dissolves and keeps the solution at a nearly uniform strength. The cyanide of potassium in the solution is sometimes replaced by ferrocyanide of potassium, and the cyanide of gold by sesquioxide of gold, chloride of gold and potassium, or sulphide of gold; but the composition above given is that which is most generally adopted. This mode of gilding may be at once applied to copper, brass, bronze, silver, or platinum. To gild iron, steel, or tin, it is necessary first to deposit a layer of copper on the surface, which is effected by immersion for a few seconds in a bath of cyanide of copper and potassium.

Electro-silvering or *electro-plating* is performed in a similar manner, with a bath composed of 1 part of cyanide of silver and 10 parts of cyanide of potassium dissolved in 100 parts of water; it is principally applied to articles made of nickel-silver.

Platinum may also be deposited in a similar manner on copper or silver; but it does not adhere very firmly.

ESTIMATION OF GOLD, AND METHODS OF SEPARATING IT FROM OTHER METALS.

Gold is always estimated in the metallic state. It is generally precipitated from its solution in aqua-regia by protosulphate of iron or oxalic acid. Protosulphate of iron precipitates the gold in the form of a fine brown powder. If the gold solution is quite neutral, it must first be acidulated with hydrochloric acid, otherwise the precipitated gold will be contaminated with sesquioxide of iron formed by the action of the air on the solution of the protosulphate. If the gold solution contains much free nitric acid, there is a risk of some of the precipitated gold being redissolved by the aqua-regia present. To prevent this, the excess of nitric acid must be destroyed by adding hydrochloric acid, and boiling before the iron solution is added. Oxalic acid reduces gold slowly but completely; the gold solution must be digested with it for 24 or 48 hours.

These methods of precipitation serve to separate gold from most other metals. In such cases, oxalic acid is mostly to be preferred as the precipitating agent, because, when the quantities of the other metals are also to be determined, the presence of a large amount of iron in solution is very inconvenient.

The separation of gold in alloys may generally be effected by dissolving out the baser metals with nitric, or sometimes with hydrochloric or sulphuric acid. When, however, the proportion of gold is considerable, it may happen that the alloy is but very slowly attacked by nitric acid, especially if the other metal be silver or lead. In such a case, it is best to treat the alloy with aqua-regia, and precipitate the gold with oxalic acid. Or, again, the alloy may be fused with a known weight of lead or silver, as in the method of quartation (p. 349.), and thereby rendered decomposable by nitric acid.

The analysis or *assay* of an alloy of gold and copper is usually made by cupellation with lead. The weight of the button remaining on the cupel gives directly the amount of gold in the alloy after certain corrections similar to those required in the case of silver (p. 348.). Alloys containing both silver and copper are cupelled with lead and a quantity of silver sufficient to bring the proportion of gold and silver in the alloy to 1 part gold and 3 parts silver. The button obtained by cupellation then consists of an alloy of gold and silver, from which the silver may be dissolved out by nitric acid.

Small ornamental articles, which would be destroyed if submitted to any of the preceding processes, are approximately assayed by rubbing them on a peculiar kind of black stone, called the *touchstone*, so as to leave a streak of metal, the appearance of which may be compared with that of similar streaks produced from alloys of known composition. A further comparison is obtained by examining the appearance which the streaks present when treated with acids. This method is also sometimes used in the assaying of coins, to afford an indication of the quantity of silver required in the cupellation. The touchstone, which is a peculiar kind of bituminous quartz, was originally obtained from Lydia; but stones of similar quality are now found in Bohemia, Saxony, and Silesia.

ORDER IX.

METALS IN NATIVE PLATINUM.

SECTION I.

PLATINUM.

Eq. 98·68 *or* 1233·5; Pt.

This metal was discovered in the auriferous sand of certain rivers in America. Its name is a diminutive of *plata*, silver, and was applied to it on account of its whiteness. It occurs in the form of rounded or flattened grains of a metallic lustre. It has been found in Brazil, Colombia, Mexico, St. Domingo, and on the eastern declivity of the Ural chain; in small quantity also in certain copper-ores from the Alps; it is everywhere associated with the debris of a rock, easily recognised as belonging to one of the earliest volcanic formations.

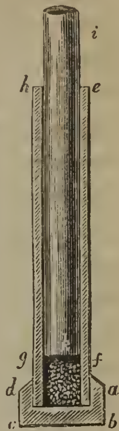
The grains of native platinum contain from 75 to 87 per cent. of that metal, a quantity of iron generally sufficient to render them magnetic, from $\frac{1}{3}$ to 1 per cent. of palladium, but sometimes much less, with small quantities of copper, rhodium, osmium, iridium, and ruthenium. To separate the platinum from these bodies, the ore is digested in a retort with hydrochloric acid, to which additions of nitric acid are made from time to time. When the hydrochloric acid is nearly saturated, the liquid is evaporated in the retort to a syrup, then diluted with water, and drawn off from the insoluble residue. If the mineral is not completely decomposed, more aqua-regia is added and the distillation continued. A portion always remains undissolved, consisting of grains of a compound of

osmium and iridium, and little brilliant plates of the same alloy, besides foreign mineral substances which may be mixed with the ore. The solution is generally deep red, and emits chlorine from the presence of perchloride of palladium; to decompose which the liquid is boiled, whereupon chlorine escapes, and the palladium is reduced to protochloride. Chloride of potassium is then added, which precipitates the platinum as a sparingly soluble double chloride of platinum and potassium, which has a yellow colour if pure, but red if it is accompanied by the double chloride of iridium and potassium. The precipitate is collected on a filter, and washed with a dilute solution of chloride of potassium. By igniting this double salt with twice its weight of carbonate of potash to the point of fusion, the platinum is reduced to the metallic state, while a portion of the iridium remains as peroxide. The soluble potash-salts are then removed by washing with hot water, and the platinum is dissolved by aqua-regia, in which the peroxide of iridium remains untouched. To complete the separation of the iridium, the precipitation by chloride of potassium and ignition with carbonate of potash may require to be repeated several times. The platinum-solution thus freed from iridium is mixed with sal-ammoniac, which throws down a yellow precipitate of the double chloride of platinum and ammonium. From this precipitate, when heated to redness, chlorine and sal-ammoniac are given off, and the platinum remains in the form of a loosely coherent mass, called *spongy platinum.* When it is not required to have platinum absolutely pure, the solution first obtained from the ore is precipitated by sal-ammoniac, and the precipitate treated in the manner just described: much of the platinum of commerce is obtained in that way. The small trace of iridium which is left in commercial platinum greatly increases its hardness and tenacity.

Platinum is too refractory to be fused in coal furnaces: but at a high temperature its particles cohere like those of iron,

and it may, like that metal, be welded, and thereby rendered malleable. For this purpose, the spongy platinum obtained by igniting the double chloride of platinum and ammonium, is introduced into a brass cylinder *e f g h* (*Fig.* 20), the lower part of which fits into a steel socket *a b c d*. The cylinder being half filled with spongy platinum, a steel piston *i k*, which fits it exactly, is introduced, and driven down by blows of a hammer, gently at first, but afterwards with greater force. The spongy platinum is thereby much reduced in bulk, and after a while is converted into a coherent disc of metal. This disc is heated to whiteness in a muffle, and afterwards hammered on a steel anvil. By repeating these operations several times, the platinum is rendered perfectly malleable and ductile, and may be rolled into sheets. Platinum in this state is the densest body at present known; its specific gravity was fixed by Dr. Wollaston at 21·53. This metal may be fused by the oxyhydrogen blow-pipe, or even made to boil, and be dissipated with scintillations. It is not acted upon by any single acid, not even by concentrated and boiling sulphuric acid. Its resistance to the action of acids, conjoined with its difficult fusibility, renders platinum invaluable for chemical experiments, and for some purposes in the chemical arts, particularly for the concentration of oil of vitriol.

Fig. 19.



The remarkable influence of a clean surface of platinum in determining the combustion of oxygen and hydrogen, has already been considered. This property platinum shares with osmium, iridium, palladium, and rhodium. It is exhibited in the greatest degree by the highly divided metal, such as platinum-sponge, the condition in which the metal is left on igniting the double chloride of platinum and ammonium. Platinum precipitated from solution by zinc, causes the com-

bustion of alcohol vapour. The *black powder of platinum*, commonly called *platinum-black*, is the form in which that metal is most active. This is prepared by dissolving the protochloride of platinum in a hot and concentrated solution of potash, and pouring alcohol into it while still hot, by small quantities at a time; violent effervescence then occurs from the escape of carbonic acid gas, by which the contents of the vessel, unless capacious, may be thrown out. The liquor is decanted from the black powder which appears, and the latter boiled successively with alcohol, hydrochloric acid, and potash, and finally four or five times with water, to divest it of all foreign matters. Platinum-black may also be obtained by decomposing a hot solution of sulphate of platinum with alcohol; and by boiling a solution of the bichloride with carbonate of soda and sugar; chloride of sodium is then formed, water and carbonic acid are produced by oxidation of the sugar, and the platinum is precipitated in the finely-divided state. The powder, when dried, resembles lamp-black, and soils the fingers, but still it is only metallic platinum extremely divided, and may be heated to full redness without any change of appearance or properties. It loses these properties, however, by the effect of a white heat, and assumes a metallic aspect. Platinum-black, like wood charcoal, absorbs and condenses gases in its pores, with evolution of heat, a property which must assist its action on oxygen and hydrogen, although not essential to that action. When moistened with alcohol, it determines the oxidation of that substance in air, and the formation of acetic acid; and, in a similar manner, it converts wood-spirit into formic acid.

Platinum is insoluble in all acids except aqua-regia. It may be oxidated in the dry way by fusing it with hydrate of potash or nitre. Palladium, osmium, and iridium resemble platinum in their chemical relations, the corresponding compounds of these four metals being isomorphous; platinum and iridium have also the same atomic weight. Of platinum,

only two degrees of oxidation are known with certainty, the protoxide, PtO, and binoxide, PtO_2.

Protoxide of platinum, Platinous oxide, PtO, 106·68 *or* 1333·5.— This oxide is obtained by digesting the corresponding chloride of platinum with potash, as a black powder, which is a hydrate. It is dissolved by an excess of the alkali, and forms a green solution, which may become black like ink with a large quantity of oxide. Protoxide of platinum forms the platinous class of salts, which have a greenish, or, sometimes red colour, and are distinguished from the platinic salts by not being precipitated by sal-ammoniac. With *hydrosulphuric acid* and *hydrosulphate of ammonia,* they form a black precipitate, soluble in a large excess of the latter; with *mercurous nitrate,* a black precipitate; with *potash,* no precipitate; with *carbonate of potash or soda,* a brownish precipitate. *Ammonia* added to the hydrochloric acid solution throws down a green crystalline precipitate of ammonio-platinous chloride; carbonate of ammonia forms no precipitate.

Protosulphide of platinum, PtS, is thrown down as a black precipitate, when the protochloride of platinum is decomposed by hydrosulphuric acid. It may be washed and dried without decomposition.

Protochloride of platinum, Platinous chloride, PtCl, is obtained by evaporating a solution of the bichloride of platinum to dryness; triturating the dry mass; and heating it in a porcelain capsule by a sand-bath at the melting point of tin, taking care to stir it at the same time, so long as chlorine is evolved. It remains as a greenish grey powder, quite insoluble in water, and repelling that liquid so as not to be moistened by it. This chloride is not decomposed by sulphuric or nitric acid, but is partially soluble in boiling and concentrated hydrochloric acid. From the last solution, alkalies throw down a black precipitate of protoxide. When the calcination of the bichloride of platinum, at 420° or 460°, is interrupted before the whole of the chlorine is expelled, the residue yields to

water a compound of a brown colour, so deep, that the liquid becomes opaque. This, Professor Magnus believes to be a combination of the two chlorides of platinum. A double *protochloride of platinum and potassium*, or *chloroplatinite of potassium*, PtCl . KCl, is obtained on adding chloride of potassium to the solution of platinous chloride in hydrochloric acid, and evaporating the liquid. The salt crystallises in red four-sided prisms, the form of which is the same as that of a corresponding salt of palladium; it is anhydrous. A protochloride of platinum and sodium also exists, but does not crystallise easily.

Corresponding *platinous iodides* and *cyanides* have been formed. The cyanide forms a numerous class of double salts, called *platinocyanides*, whose general formula is MCy.PtCy. The potassium salt is obtained by heating spongy platinum with ferrocyanide of potassium; exhausting the mass with hot water and crystallising; or by treating platinous chloride with aqueous cyanide of potassium. The salt crystallises in needles and rhombic prisms, pale yellow by transmitted light, yellow or blue by reflected light, according to the direction in which they are viewed. From the solution of this salt, the platino-cyanides of zinc, lead, copper, mercury, and silver, which are insoluble, are obtained by precipitation. The sodium, barium, strontium, and calcium-salts, which are soluble, are obtained by treating the copper-salt with caustic soda, baryta, &c.; and the magnesium and aluminum-salts, by precipitating the barium-salt with sulphate of magnesia or alumina. The ammonium-salt is prepared like the potassium-salt. Platinous oxide has also been united with several acids, particularly sulphuric, nitric, oxalic, and acetic acids; but none of these salts have been crystallised, except the oxalate.

Bioxide of platinum, Peroxide of platinum, Platinic oxide, PtO_2, 114·68 *or* 1433·5.—By precipitating sulphate of platinum with nitrate of baryta, nitrate of platinum is obtained.

One half of its oxide may be precipitated by soda, from the last salt, but when a larger quantity of alkali is added, a sub-salt is thrown down. The precipitated oxide is hydrated, very bulky, and exactly resembles sesquioxide of iron precipitated by ammonia. When heated, it first loses its water, and becomes black, then its oxygen, and leaves metallic platinum. Bioxide of platinum combines with acids, and forms a class of salts, which are either yellow or reddish-brown. From the solutions of these salts, the platinum is precipitated in the metallic state by *phosphorus* and by most *metals*. *Hydrosulphuric acid* and *sulphide of ammonium* form a black precipitate soluble in a large excess of the latter. In a solution of platinic chloride, *potash* or *ammonia* forms a yellow crystalline precipitate of chloroplatinate of potassium or ammonium; so likewise do the *chlorides of potassium* or *ammonium*; sodium-salts form no precipitate. In the solution of platinic nitrate or sulphate, *potash* or *ammonia* forms a yellow-brown precipitate; *chloride of potassium* or *ammonium* produces, after some time, a slight yellow precipitate of the double chloride. Platinic oxide has also a decided affinity for bases, and forms insoluble compounds with the alkalies, earths, and many metallic oxides. It forms also, like sesquioxide of gold, a fulminating ammoniacal compound, discovered by Mr. E. Davy.

Bisulphide of platinum, PtS_2, is formed by adding a solution of bichloride of platinum, drop by drop, to a solution of sulphide of potassium. It is dark brown and becomes black by desiccation. When dried in open air, a portion of its sulphur is converted into sulphuric acid, by absorption of oxygen, and the mass becomes strongly acid.

Bichloride of platinum, $PtCl_2$, 2121 *or* 169·68, is obtained by concentrating the solution of platinum in aqua-regia, as a red saline mass, which becomes brown when deprived of its water of crystallisation by heat. The solution of this salt when pure has an intense and unmixed yellow colour, the red

colour which it usually exhibits being due to iridium or to protochloride of platinum. Bichloride of platinum is soluble in alcohol, and the solution is used to separate potash and ammonia in analysis.

Chloride of platinum and potassium, Chloroplatinate of potassium, $KCl \cdot PtCl_2$, is the salt which falls on mixing chloride of platinum with chloride of potassium or any other salt of potash. The crystalline grains of which it is composed are regular octohedrons. This salt is soluble to a certain extent in water, but is wholly insoluble in alcohol. It is anhydrous. A very intense red-heat is required for its complete decomposition. *Chloroplatinate of sodium,* $NaCl \cdot PtCl_2 + 6HO$, crystallises in beautiful transparent prisms of a bright yellow colour. It is soluble in alcohol as well as in water. When a solution of this salt in alcohol is distilled till only one-fourth of the liquid remains, the solution yields by evaporation a salt containing the elements of ether, and belonging to a class of compounds discovered by Professor Zeise, and known as the etherised salts of Zeise.

Chloroplatinate of ammonium resembles the double salt of potassium. When ignited, it leaves metallic platinum in the spongy state. Bonsdorff has formed a large class of compounds of bichloride of platinum with the alkaline, earthy, and metallic chlorides, in all of which the salts are united in single equivalents. The bromides and iodides of platinum have likewise been formed, and classes of double salts derived from them. Bioxide of platinum has also been combined with acids; but none of its salts, with the exception of the oxalate, is obtained in a crystalline state.

Bicyanide of platinum, or *platinic cyanide,* does not appear to exist in the separate state; but it forms double salts with the cyanides of potassium and ammonium; it likewise combines with chloride of potassium, forming the compound $KCl \cdot PtCy_2$.

The *sulphocyanides of platinum,* $PtCyS_2$, and $Pt \cdot (CyS_2)_2$.

likewise form two series of double salts, viz. the *platino-bisulphocyanides* or *sulphocyanoplatinites* = $MPt(CyS_2)_2$, or $MCyS_2 + PtCyS_2$, and the *platino-tersulphocyanides* or *sulpho-cyanoplatinates* = $MPt(CyS_2)_3$, or $MCyS_2 + Pt(CyS_2)_2$. The potassium salts are formed by the action of sulphocyanide of potassium on protochloride and bichloride of platinum respectively. All these salts are strongly coloured, exhibiting all shades of colour from light yellow to deep red. They are quickly decomposed by heat (G. B. Buckton).*

AMMONIACAL PLATINUM SALTS.

The oxides, chlorides, sulphates, &c., of platinum are capable of taking up the elements of 1 or 2 equivalents of ammonia, giving rise to four series of compounds, whose composition may be represented by the following general formulæ, in which the symbols R, R′ denote acid elements:

1. Ammonio-platinous compounds, or protosalts of platammonium,

$$NH_3PtR = \overbrace{NH_3Pt}\,.\,R.$$

2. Biammonio-platinous compounds, or protosalts of ammo-platammonium,

$$N_2H_6PtR = \overbrace{NH_2(NH_4)Pt}\,.\,R.$$

3. Ammonio-platinic compounds, or bisalts of platammonium,

$$NH_3Pt\begin{cases} R_2 \\ \text{or } RR' \end{cases} = \overbrace{NH_3Pt}\,.\begin{cases} R_2 \\ \text{or } RR'. \end{cases}$$

4. Biammonio-platinic compounds, or bisalts of ammo-platammonium,

$$N_2H_6Pt\begin{cases} R_2 \\ \text{or } RR' \end{cases} = \overbrace{NH_2(NH_4)Pt}\,.\begin{cases} R_2 \\ \text{or } RR'. \end{cases}$$

The third and fourth classes of these compounds may also be regarded as protosalts of compound ammoniums, in which

* Chem. Soc. Qu. J. vii. 22.

1 eq. of hydrogen is replaced by PtO or PtCl; for example, the bichloride $NH_3PtCl_2 = N\overbrace{H_3(PtCl)} . Cl$; the chloronitrate $N_2H_6PtClNO_6 = N\overbrace{H_2(NH_4)PtCl} . NO_6$.

1. *Ammonio-platinous compounds, or Protosalts of Platammonium.* — These compounds are formed by the action of heat on those of the following series, half the ammonia of the latter being then given off. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the biammoniacal platinous compounds; they detonate when heated.

Oxide, $NH_3PtO = N\overbrace{H_3Pt} . O$.—Obtained by heating the hydrated oxide of biammo-platammonium to 230°. It is a greyish mass which, when heated to 392° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. Probably the compound, Pt_3N, is first produced and is afterwards resolved into nitrogen and platinum:

$$3NH_3PtO = Pt_3N + 3HO + 2NH_3.$$

The oxide, heated to 392° in contact with the air, becomes incandescent, and burns vividly, leaving a residue of platinum.

Chloride, $NH_3PtCl = N\overbrace{H_3Pt} . Cl$. — Of this compound three isomeric modifications exist: α. *Yellow*, obtained by adding hydrochloric acid, or a soluble chloride, to a solution of nitrate or sulphate of platammonium. Or, by boiling the green modification, γ, with nitrate or sulphate of ammonia, whereupon it dissolves and forms a solution which, on cooling, deposits the yellow salt. Or, by neutralising a solution of platinous chloride in hydrochloric acid with carbonate of ammonia, heating the mixture to the boiling point, and adding a quantity of ammonia equal to that already contained in the liquid, filtering from a dingy green substance, which deposits after a while, then leaving the solution to cool, and decanting the supernatant liquid as soon as the yellow salt is

deposited. *β. Red.*—If, in the last mode of preparation, the carbonate of ammonia, instead of being added at once in excess, be added drop by drop to the hydrochloric acid solution of platinous chloride, the liquid on cooling deposits small garnet-coloured crystals having the form of six-sided tables. This red modification may also be obtained in other ways (Peyrone).* *γ. Green.* — This modification, usually denominated the *green salt of Magnus,* was the first discovered of the ammoniacal platinum compounds. It is obtained by gradually adding an acid solution of platinous chloride to caustic ammonia, or by passing sulphurous acid gas into a boiling solution of bichloride of platinum till it is completely converted into protochloride (and therefore no longer gives a precipitate with sal-ammoniac), and neutralising the solution with ammonia ; the compound is then deposited in green needles. The same modification of the salt may also be obtained by adding an acid solution of platinous chloride to a solution of biammonio-platinous chloride, N_2H_6PtCl. Hence it would appear that the true formula of this green salt is $(NH_3PtCl)_2 = PtCl + N\overbrace{H_2(NH_4)Pt}.Cl$, that of the yellow or red modification being simply NH_3PtCl. Either modification of the salt, when heated to 572°, gives off nitrogen, hydrochloric acid, and sal-ammoniac, and leaves a residue of platinum.

A red crystalline compound of chloride of platammonium with chloride of ammonium, viz. $NH_3PtCl + NH_4Cl$, is formed when a solution of chloride of ammo-platammonium, containing a large quantity of sal-ammoniac, is evaporated to the crystallising point. Thus, when a solution of platinous chloride in hydrochloric acid is precipitated by ammonia, and the green salt of Magnus thereby formed is heated, while still in the liquid, with excess of ammonia, to convert it into chloride of ammo-platammonium, the red compound separates at a

* Vide Translation of Gmelin's Handbook, vi. 303.

certain degree of concentration, together with the chloride of ammo-platammonium (Grimm).*

Iodide, NH_3PtI.—Yellow powder, obtained by boiling the aqueous solution of the compound N_2H_6PtI. It dissolves in ammonia, and is thereby reconverted into the latter compound.

Cyanide, NH_3PtCy.—Obtained by adding hydrocyanic acid to a solution of biammonio-platinous oxide, cyanide of ammonium being formed at the same time (Reiset):

$$N_2H_6PtO + 2HCy = NH_3PtCy + NH_4Cy + HO.$$

Also, by digesting ammonio-platinous chloride with cyanide of silver. It crystallises in fine regular needles of a pale yellow colour, soluble with tolerable facility in water and ammonia. An isomeric modification of this compound, $(NH_3PtCy)_2 = N_2H_6PtCy + PtCy$, is formed by passing cyanogen gas into a moderately concentrated solution of biammonio-platinous oxide; the cyanogen then decomposes the water, forming hydrocyanic and cyanic acids, and the hydrocyanic acid acts upon the biammonio-platinous oxide, forming the compound $(NH_3PtCy)_2$, together with ammonia and water:

$$2(N_2H_6PtO) + 2HCy = (NH_3PtCy)_2 + 2NH_3 + 2HO.$$

The compound, $(NH_3PtCy)_2$, crystallises out and may be purified by recrystallisation from water. It is also obtained by mixing a solution of biammonio-platinous chloride with cyanide of potassium. It forms crystals which, under the microscope, appear like six-sided tables arranged in stellate groups; it dissolves without decomposition in potash, hydrochloric acid, and dilute sulphuric acid, but is decomposed by strong sulphuric and by nitric acids (Buckton).†

The sulphate, $NH_3Pt.SO_4.HO$, and the *nitrate,* $NH_3Pt.NO_6$, are obtained by boiling the iodide with sulphate and nitrate

* Ann. Ch. Pharm. xcix. 95.

† Chem. Soc. Qu. J., iv. 34.

of silver; they are crystalline, and have a strong acid reaction. The sulphate retains one atom of water, which cannot be removed without decomposing the salt.

2. *Biammonio-platinous compounds, or Protosalts of Ammoplatammonium.*—*Oxide*, $N_2H_6PtO \, . \, HO = N\overbrace{H_2(NH_4)Pt} \, . \, O + HO$.—Obtained by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in vacuo; a crystalline mass is then left, containing $N_2H_6PtO \, . \, HO$. The oxide is not known in the anhydrous state. The hydrate is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates oxide of silver from the solution of the nitrate. It is a strong base, neutralising acids completely, and expelling ammonia from its salts. It melts at 230°, giving off water and ammonia, and leaving the compound NH_3PtO. Its aqueous solution does not give off ammonia, even when boiled.

Chloride, $N_2H_6PtCl = N\overbrace{H_2(NH_4)Pt} \, . \, Cl$.—This compound is prepared by boiling protochloride of platinum, or the green salt of Magnus, with aqueous ammonia, till the whole is dissolved, and evaporating the liquid to the crystallising point. Or, by passing sulphurous acid gas into bichloride of platinum till the solution is completely decolorised, precipitating with carbonate of soda, dissolving the precipitate of sodio-platinous sulphite in hydrochloric acid, saturating the resulting solution of chloride of sodium and platinous chloride with ammonia, and dissolving the precipitate of N_2H_6PtCl and NH_3PtCl in boiling hydrochloric acid. The filtered liquid on cooling deposits NH_3PtCl, while the biammoniacal compound remains in solution and may be obtained by evaporation, mixed however, with sal-ammoniac. It separates in bulky crystals of a faint yellow colour, containing 1 eq. water, which is completely given off at 230°. At 482° it gives off ammonia, and leaves NH_3PtCl. The anhydrous compound rapidly absorbs

water from the air. The hydrate does not give off ammonia when treated with caustic alkalies in the cold, and is but very slowly decomposed by them, even with the aid of heat.

Chloride of ammo-platammonium forms two compounds with bichloride of platinum. The first, whose formula is $2(\overbrace{NH_2(NH_4)Pt}.Cl) + PtCl_2$, is obtained as an olive-green precipitate on adding bichloride of platinum to a solution of $\overbrace{NH_2(NH_4)Pt}.Cl$; the second, $\overbrace{NH_2(NH_4)Pt}.Cl + PtCl_2$, by treating the preceding with excess of bichloride of platinum.

The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallise in cubes.

The *sulphate*, $\overbrace{NH_2(NH_4)Pt}.SO_4$, and the *nitrate*, $NH_2(NH_4)Pt.NO_6$, are obtained by decomposing the chloride with sulphate or nitrate of silver; they are neutral, and crystallise easily.

Carbonates.—The hydrated oxide absorbs carbonic acid rapidly from the air, forming first, a neutral carbonate, $\overbrace{NH_2(NH_4)Pt}.CO_3 + HO$, and afterwards an acid salt, $\overbrace{NH_2(NH_4)Pt}.CO_3 + CO_3H$.

3. *Ammonio-platinic compounds; or, Bi-salts of platammonium.*—The *oxide*, $NH_3PtO_2 = \overbrace{NH_3Pt}.O_2$, may also be regarded as *oxide of oxyplatammonium*, $\overbrace{NH_3(PtO)}.O$. It is obtained by adding ammonium to a boiling solution of ammonio-platinic nitrate; it is then precipitated in the form of a heavy, yellowish, crystalline powder, composed of small, shining, rhomboidal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic

acid, and forms a large number of crystallisable salts, both neutral and acid, having a yellow colour, and sparingly soluble in water (Gerhardt).* Another compound of platinic oxide with ammonia, called *fulminating platinum,* whose composition has not been exactly ascertained, is produced by decomposing chloroplatinate of ammonium with aqueous potash. It is a straw-coloured powder which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

Chloride, $NH_3PtCl_2 = \overbrace{NH_3Pt}.Cl_2 = \overbrace{NH_3\,(PtCl)}.Cl$. — Obtained by passing chlorine gas into boiling water in which the compound NH_3PtCl (the yellow modification) is suspended. This compound is insoluble in cold water, and very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of biammoniacal platinic chloride. The compound $NH_3Pt.Cl_2$ dissolves in boiling potash without evolving ammonia. An isomeric compound,

$$(NH_3PtCl_2)_2 = N_2H_6PtCl_2 + PtCl_2,$$

is obtained by passing chlorine into water in which Magnus's green salt is suspended. A red crystalline powder is at first precipitated, consisting of $N_2H_6PtCl + PtCl_2$; but on continuing the passage of the chlorine, this precipitate redissolves, and the solution yields, by evaporation, the crystalline compound $(NH_3PtCl_2)_2$.

The *sulphate,* $NH_3Pt.(SO_4)_2$, is obtained by dissolving the oxide in dilute sulphuric acid, and evaporating. It is a yellow powder, having an acid taste, and is soluble in boiling water.

Nitrates. — A *mononitrate,* $NH_3PtO_2.NO_5 + 3HO$, or *oxynitrate,* $\overbrace{NH_3Pt}.\left\{\begin{matrix}NO_6\\O\end{matrix}\right. + 3HO$, or *nitrate of oxyplat-*

* Comptes Rendus des Travaux de Chimie, 1849, p. 273.

ammonium, $NH_3\overbrace{(PtO)}$. $NO_6 + 3HO$, is obtained by boiling the chloride NH_3PtCl_2 for several hours with a dilute solution of nitrate of silver. It is a yellow, crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *binitrate*, $N\overbrace{H_3Pt}$. $2NO_6 + 2HO$, is obtained by dissolving the mononitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxalate*, $NH_3PtO_2 . C_2O_3 + 2HO$, or $NH_3Pt\left\{\begin{matrix} C_2O_4 \\ O \end{matrix}\right. +$ $2HO$, or $N\overbrace{H_3 (PtO)}. C_2O_4 + 2HO$, is formed by decomposing the nitrate with oxalate of ammonia. It is a light yellow precipitate, soluble in boiling water, and detonating when heated.

4. *Biammonio-platinic compounds*, or *Bi-salts of ammoplatammonium.* — The oxide of this series has not yet been isolated.

Chloride. — $N_2\ H_6\ Pt\ Cl_2 = N\ \overbrace{H_2 (N\ H_4)\ Pt} . Cl_2 =$ $\overbrace{N H_2 (N H_4) (PtCl)} . Cl.$ — Obtained by passing chlorine gas into a solution of biammonio-platinous chloride, N_2H_6PtCl; by dissolving ammonio-platinic chloride, NH_3PtCl_2, in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of one of the nitrates,

$$N_2H_6PtO_2 . NO_5, \text{ or } N_2H_6PtClO . NO_5,$$

with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent, regular octohedrons, having a faint yellow tint. When a solution of this salt is treated with nitrate of silver, one half of the chlorine is very easily precipitated, but to remove even a small portion of the remainder requires a long-continued action of the silver-salt; a result easily explained if the salt be regarded as a chlo-

ride of ammo-chlorplatammonium, $\overbrace{NH_2(NH_4)(PtCl)}.Cl$ (Grimm.)* A compound having the formula N_2H_5PtCl, containing, therefore, 1 eq. Cl and 1 eq. H less than the preceding, is obtained by dissolving chloroplatinate of ammonium in ammonia, and precipitating by alcohol; but it does not crystallise, merely drying up to a pale yellow, resinous mass: hence its composition is doubtful.

Nitrates.—A mononitrate, $N_2H_6PtO_2.NO_5$, or oxynitrate of ammoplatammonium, $\overbrace{NH_2(NH_4)Pt}\left\{\begin{matrix}NO_6\\O\end{matrix}\right.$, or nitrate of ammoxyplatammonium, $\overbrace{NH_2(NH_4)(PtO)}.NO_6$, is obtained by boiling the following salt *b*, with ammonia: it is a white amorphous powder, slightly soluble in cold, more soluble in boiling water.

Sesquinitrate, $2(N_2H_6PtO_2).3NO_5$, or

$$2\left(\overbrace{NH_2(NH_4)Pt}\right).\left\{\begin{matrix}3NO_6\\O\end{matrix}\right., \text{ or } \left.\begin{matrix}\overbrace{NH_2(NH_4)(PtO)}\\\overbrace{NH_2(NH_4)(PtNO_6)}\end{matrix}\right\}2NO_6.—$$

Formed by boiling the mononitrate of ammoplatammonium with nitric acid. It is a colourless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid (Gerhardt).

Chloronitrates.—*a.* $N_2H_6PtClO.NO_5$; or $\overbrace{NH_2(NH_4)Pt}.\left\{\begin{matrix}NO_6\\Cl,\end{matrix}\right.$ or $\overbrace{NH_2(NH_4)(PtCl)}.NO_6$.—This salt was discovered by Gros. It is obtained by treating Magnus's green salt with strong nitric acid. The green compound first turns brown, and is afterwards converted into a mixture of platinum and a white powder, which is dissolved out by boiling water, and crystallises on cooling in shining flattened prisms, colourless, or having a pale yellow tint. The reaction may be thus represented:—

$$2(NH_3PtCl) + HO.NO_5 = N_2H_6PtCl.NO_6 + Pt + HCl.$$

* Ann. Ch. Pharm. xcix. 77.

This compound dissolves readily in water, especially when heated. The chlorine and platinum contained in the solution cannot be detected by the ordinary reagents; thus, nitrate of silver and hydrosulphuric acid yield but very trifling precipitates, even after a long time.

$$b.\ 4NH_3 \cdot Pt_2ClO_3 \cdot 2NO_5, \text{ or } \left.\begin{array}{l}\overbrace{NH_2(NH_4)(PtCl)}\\ \overbrace{NH_2(NH_4)(PtCl)}\end{array}\right\} \cdot 2NO_6.$$

Discovered by Raewsky. When Magnus's green salt is boiled with a large excess of nitric acid, red fumes are evolved, and the resulting solution deposits this salt in small, brilliant, needle-shaped prisms, which deflagrate when heated, giving off water and chloride of ammonium, and leaving metallic platinum. Raewsky assigns to this salt the formula $4NH_3 \cdot Pt_2ClO_5 \cdot 2NO_5$; but the formula above given, which is deduced from Gerhardt's analysis, and contains 2O less, is much more probable, as it accords with the constitution of the other compounds of the series. The 2 atoms of nitric acid contained in this salt may be replaced by 2 atoms of *carbonic* or *oxalic* acid, yielding sparingly soluble crystalline salts of exactly similar constitution. There is also a *phosphate* containing $4NH_3 \cdot Pt_2ClO_3 \cdot PO_5 \cdot HO$, obtained by mixing the solution of the nitrate with ordinary phosphate of soda. According to Raewsky, the mother-liquor from which the preceding nitrate has crystallised, contains another nitrate whose formula is $4NH_3 \cdot Pt_2Cl_2O_4 \cdot 2NO_5$; but Gerhardt finds this salt to be identical with the nitrate discovered by Gros.

Chlorosulphate, $N_2H_6PtClSO_4 = \overbrace{NH_2(NH_4)(PtCl)} \cdot SO_4$.—Obtained by treating biammonio-platinic chloride, or Gros's nitrate, with dilute sulphuric acid, or by mixing the solution of the nitrate with a strong solution of a soluble sulphate. It crystallises in slender needles, sparingly soluble in cold water, but dissolving with tolerable facility in boiling water. The

sulphuric acid in the solution is not precipitated by baryta-salts. The salt is, however, decomposed by hydrochloric or nitric acid, either of which takes the place of the sulphuric acid, reproducing the chloride or nitrate (Gros).

Chloroxalate, $N_2H_6PtClO \,.\, C_2O_3 = \widehat{NH_2(NH_4)Pt}\left\{\begin{matrix} C_2O_4 \\ Cl \end{matrix}\right. =$ $\widehat{NH_2(NH_4)(PtCl)} \,.\, C_2O_4$.—Oxalic acid or an alkaline oxalate added to the solution of the corresponding sulphate or nitrate, throws down this salt in the form of a white granular precipitate, insoluble in water.

Oxalonitrates. — *a.* $N_2H_6PtO_2 \,.\, NO_5 \,.\, C_2O_3 =$

$$\widehat{NH_2(NH_4)Pt}.\left\{\begin{matrix} NO_6 \\ C_2O_4 \end{matrix}\right. = \widehat{NH_2(NH_4)(PtNO_6)} \,.\, C_2O_4.$$

Deposited as a white crystalline body from a solution of the following salt *b* in dilute nitric acid.

b. $2(N_2H_6PtO_2) \,.\, NO_5 \,.\, 2C_2O_3 = 2(\widehat{NH_2(NH_4)Pt}) \,.\left\{\begin{matrix} 2C_2O_4 \\ NO_6 \\ O \end{matrix}\right. =$

$\left.\begin{matrix} \widehat{NH_2(NH_4)(PtO)} \\ NH_2(NH_4)(PtNO_6) \end{matrix}\right\} 2C_2O_4$.—Obtained by adding oxalate of ammonia to a solution of the sesquinitrate; it is insoluble in water (Gerhardt).

GERHARDT'S THEORY OF THE AMMONIACAL PLATINUM COMPOUNDS.

These compounds may be regarded as salts of peculiar bases or alkalies, formed from ammonia by the substitution of one or two atoms of platinum for hydrogen; admitting, however, that platinum (like other metals) may enter into its compounds with two different equivalent weights, viz., in the platin*ous* compounds, as *Platinosum* = 98·68 = Pt, and in the platin*ic* compounds, as *Platinicum* = 49·34 = pt. This being admitted, the ammonio-platinous compounds may be regarded as salts of an alkali, called *Platosamine* = NH_2Pt, formed from ammonia by the substitution of 1 atom of platinosum for 1 atom of hydrogen; and the biammonio-platinous compounds,

as salts of *Diplatosamine* = N_2H_5Pt, formed by the union of two atoms of ammonia into one, and the substitution therein of 1 Pt for 1 H: thus for the chlorides:—

$$NH_3PtCl = \text{Hydrochlorate of Platosamine} = NH_2Pt . HCl;$$

$$N_2H_6PtCl = \text{Hydrochlorate of Diplatosamine} = N_2H_5Pt.HCl;$$

and for the nitrates:—

$$NH_3Pt.NO_6 = \text{Nitrate of Platosamine} = NH_2Pt . HNO_6;$$

$$N_2H_6Pt.NO_6 = \text{Nitrate of Diplatosamine} = N_2H_5Pt . HNO_6.$$

In a similar manner, the ammonio-platinic compounds may be regarded as salts of *Platinamine* = $NHpt_2$, and the biammonio-platinic compounds as salts of *Diplatinamine* = $N_2H_4pt_2$; thus—

$$NH_3PtCl_2 = \text{Bihydrochlorate of Platinamine} = NHpt_2 . 2HCl.$$

$$N_2H_6PtCl_2 = \text{Bihydrochlorate of Diplatinamine} = N_2H_4pt_2.2HCl.$$

Diplatinamine forms three kinds of salts, viz., mono-acid, sesqui-acid, and bi-acid salts; and, moreover, exhibits a peculiar tendency to form double salts containing two acids: thus, the salts discovered by Gros may be regarded as bi-acid salts, and those discovered by Raewsky, as sesqui-acid salts of diplatinamine containing hydrochloric together with another acid; thus:—

$$\text{Mononitrate} = N_2H_6PtO_2 . NO_5 = N_2H_4pt_2 . HNO_6 + HO.$$

$$\text{Sesquinitrate} = 2(N_2H_6PtO_2) . 3NO_5 = 2N_2H_4pt_2 . 3HNO_6 + HO.$$

$$\left.\begin{matrix}\text{Chloronitrate}\\ \text{(Gros's nitrate)}\end{matrix}\right\} = N_2H_6PtClO . NO_5 = N_2H_4pt_2 . \left\{\begin{matrix}HCl\\ HNO_6\end{matrix}\right.$$

$$\left.\begin{matrix}\text{Sesquichloronitrate}\\ \text{(Raewsky's nitrate)}\end{matrix}\right\} = N_4H_{12}Pt_2ClO_3.2NO_5 = 2N_2H_4pt_2 . \left\{\begin{matrix}HCl\\ 2HNO_6\end{matrix}\right. + HO.$$

$$\text{Oxalonitrate} = N_2H_6PtO_2 . NO_5 . C_2O_3 = N_2H_4pt_2 . \left\{\begin{matrix}C_2HO_4\\ HNO_6.\end{matrix}\right.$$

$$\text{Sesqui-oxalonitrate} = 2(N_2H_6PtO_2) . NO_5 . 2C_2O_3 =$$

$$2N_2H_4pt_2 . \left\{\begin{matrix}2C_2HO_4\\ HNO_6\end{matrix}\right. + HO.$$

ESTIMATION AND SEPARATION OF PLATINUM.

For quantitative estimation, platinum is usually precipitated from its solutions in the form of chloroplatinate of ammonium. The acid solution of platinum, after sufficient concentration, is mixed with a very strong solution of sal-ammoniac, and a sufficient quantity of strong alcohol added to render the precipitation complete. The precipitate of chloroplatinate of ammonium is then washed with alcohol, to which a small quantity of sal-ammoniac has been added, and then heated to redness in a weighed porcelain crucible, whereupon it is decomposed and leaves metallic platinum. Great care must, however, be taken in the ignition to prevent loss, as the evolved vapours are very apt to carry away small particles of the salt and of the reduced metal. The best mode of avoiding this source of error is to place the precipitate in the crucible *enclosed in the filter,* and expose it for some time to a moderate heat, with the cover on the crucible, till the filter is charred, and then to a somewhat higher temperature to expel the chlorine and chloride of ammonium. The crucible is then partially opened and the carbonaceous matter of the filter burnt away in the usual manner. When these precautions are duly observed, not a particle of platinum is lost. Instead of igniting the precipitate and weighing the platinum, the precipitate is sometimes collected on a weighed filter, dried over the water-bath and weighed; but this method is less accurate, because the precipitate always contains an excess of sal-ammoniac (H. Rose).

Chloride of potassium may also be used instead of chloride of ammonium to precipitate platinum, the concentrated solution of the platinum being previously mixed with a sufficient quantity of strong alcohol to bring the per centage of alcohol in the liquid to between 60 and 70 per cent. The precipitated chloroplatinate of potassium is then washed with alcohol of

60 to 70 per cent. and decomposed by simple ignition in a porcelain crucible, if its quantity is small, or in an atmosphere of hydrogen if its quantity is larger; the chloride of potassium washed out by water; and the platinum dried, ignited, and weighed.

Potash and ammonia may also be estimated by precipitating their solutions with chloride of platinum, and treating the precipitates in the manner just described. Every 100 parts of platinum correspond to 47·83 parts of potash, and 17·25 parts of ammonia.

The same methods of precipitation serve also for the separation of platinum from most of the preceding metals. To separate platinum from *silver*, when the two metals are combined in an alloy, the best method is to heat the alloy with pure and strong sulphuric acid, diluted with about half its weight of water, till the sulphuric acid begins to escape in dense fumes. The silver is thereby converted into sulphate, and the platinum remains behind in the metallic state. The sulphate of silver is dissolved by a large quantity of hot water, the platinum washed with hot water, and again treated with sulphuric acid, to separate the last traces of silver.

SECTION II.

PALLADIUM.

Eq. 53·36 *or* 665·9; Pd.

This metal was discovered in 1803 by Dr. Wollaston. It is precipitated by cyanide of mercury from the solution of the ore of platinum, after the removal of that metal by sal-ammoniac, and is gradually deposited as a yellowish white flocculent powder, which is cyanide of palladium, and yields the metal when calcined. Palladium likewise occurs, associated with a larger quantity of gold and a small quantity of

silver, in a peculiar gold-ore from Brazil, called *oropudre*. This mineral, which contains 10 per cent. of palladium, and is the chief source of that metal, is dissolved in aqua-regia, the acid solution saturated with potash, and the palladium precipitated by cyanide of mercury.

In external characters, palladium closely resembles platinum. It is nearly as infusible, but can more easily be welded. The density of the fused metal is 11·3; after being laminated, 11·8. At a certain temperature, the surface of palladium tarnishes and becomes blue from oxidation, but at a stronger heat the oxide is reduced. Palladium is very slightly attacked by boiling and concentrated hydrochloric and sulphuric acids. It dissolves in nitric acid, communicating a brownish red colour to the acid, while no gas is evolved if the temperature is low, the nitric acid being converted into nitrous acid. Palladium dissolves with facility in aqua-regia; its surface is blackened by tincture of iodine, which has no effect upon platinum.

Palladium is sometimes used for making the divided scales of astronomical instruments; being nearly as white as silver, and not blackened by sulphurous emanations, it is well adapted for that purpose. An alloy of palladium with 1-10th of its weight of silver is used by dentists.

Palladium has a much greater affinity for oxygen than platinum. It forms two oxides, the *protoxide* PdO, and the *bioxide* PdO_2.

Protoxide of palladium, Palladous oxide, PdO, 61·27 *or* 765·9.—This oxide is obtained by dissolving palladium in nitric acid, evaporating the solution to dryness, and calcining the nitrate at a gentle heat. It forms a black mass, which dissolves with difficulty in acids. When carbonate of potash or soda is added in excess to a palladous salt, the hydrated protoxide precipitates of a very dark brown colour. This oxide is easily deprived of its water by heat, but a violent calcination is necessary to reduce it to the metallic state.

The palladous salts are for the most part brown or red; their taste is astringent, but not metallic. When ignited alone, or when gently heated in hydrogen gas, they yield metallic palladium. The metal is precipitated from the solutions of palladous salts by *phosphorus*, by *sulphurous acid*, by *nitrite of potash*, by all the *metals* which reduce silver, by *formiate of potash*, and by *alcohol* at a boiling heat. *Hydrosulphuric acid* and *hydrosulphate of ammonia* throw down the brown sulphide of palladium, insoluble in the latter reagent. *Hydriodic acid* and *iodide of potassium* throw down a black precipitate of iodide of palladium, visible even to the 500,000th degree of dilution. This reaction serves for the separation of iodine from bromine; for alkaline bromides do not precipitate palladous salts. *Potash* or *soda* forms a brown precipitate of a basic salt, soluble, with the aid of heat, in excess of the reagent. *Ammonia* produces no precipitate in a solution of palladous nitrate; but from a solution of the chloride it throws down a flesh-coloured precipitate of ammonio-chloride of palladium, soluble in excess of ammonia. The *carbonates of potash* and *soda* form a brown precipitate of hydrated palladous oxide. Carbonate of ammonia acts like ammonia. *Phosphate of soda* forms a brown precipitate. *Ferrocyanide* and *ferricyanide of potassium* form no precipitates, but the liquid after a while coagulates into a jelly. *Cyanide of mercury* throws down a white precipitate of cyanide of palladium. *Protochloride of tin* forms a black precipitate, which dissolves with intense green colour in hydrochloric acid. *Protosulphate of iron* precipitates palladium slowly from the nitrate, but not from the chloride. The reactions of palladium with hydrosulphuric acid, cyanide of mercury, and iodide of potassium taken together, serve to distinguish it from all other metals.

Protosulphide of palladium, PdS, is obtained by precipitating a palladous salt by hydrosulphuric acid, and is of a dark

brown colour; it may also be prepared by the direct union of its elements.

Protochloride of palladium, PdCl, is prepared by dissolving palladium in hydrochloric acid, to which a little nitric acid is added, and evaporating the solution to dryness, to expel the excess of acid. The compound is a mass of a dark brown colour, which becomes black when made anhydrous by heat, and may be fused in a glass vessel. When heated in platinum vessels, it becomes contaminated with the protochloride of that metal. When dissolved with chloride of potassium, it forms a double salt, KCl . PdCl, which is soluble in cold, and considerably more so in hot water, and crystallises in four-sided prisms, of a dull yellow colour. Protochloride of palladium also combines with chloride of ammonium and chloride of sodium, according to Bonsdorff, and forms double salts with most other chlorides.

Protocyanide of palladium, PdCy, is always formed when cyanide of mercury is added to a neutral solution of palladium, as a light-coloured precipitate, which becomes grey after drying. When the solution of palladium is acid, no precipitate is formed, and when the solution contains copper, the precipitate has a green colour. Palladium appears to have a greater affinity for cyanogen than any other metal. Even cyanide of mercury is decomposed when boiled with protoxide of palladium, and cyanide of palladium formed. When this cyanide is dissolved in ammonia, and the excess of the latter allowed to escape by evaporation, a precipitate of brilliant, colourless, crystalline plates is formed, which appears to consist of ammoniacal cyanide of palladium.

Nitrate of palladium, $PdO . NO_5$, is formed by dissolving the metal in nitric acid; the solution dries up into a dark red saline mass. When an excess of ammonia is added to an acid solution of this salt, and the solution evaporated by a gentle heat, a colourless nitrate of palladium and ammonium is deposited in rectangular tables.

Bioxide of palladium, Peroxide of palladium, Palladic oxide, PdO_2, 69·27 *or* 865·9.—To prepare this oxide, Berzelius recommends a solution of the hydrate or carbonate of potash to be added by small quantities at a time, to the dry bichloride of palladium and potassium, mixing well after each addition. A yellowish brown powder separates, which is the hydrated bioxide, retaining a little alkali. Washed with boiling water, it loses the greater part of its combined water and becomes black. This oxide dissolves with difficulty in acids; the solutions are yellow. The corresponding bisulphide of palladium has not been formed.

Bichloride of palladium, $Pd\,Cl_2$, is obtained in solution, when the protochloride is dissolved in concentrated aqua-regia, and the solution only slightly heated. Its solution is of so dark a brown as to appear black, and gives a red precipitate with chloride of potassium. When the solution is diluted or heated, chlorine gas is evolved, and protochloride of palladium reproduced. The double salt of this chloride and chloride of potassium is obtained by treating the double protochloride of palladium and potassium in fine powder with aqua-regia, and evaporating the supernatant fluid to dryness. It forms a cinnabar red powder, in which little octohedral crystals can be perceived, both the palladic and palladous double chlorides being isomorphous with the corresponding compounds of platinum. When treated with hot water, this double salt emits chlorine, and is in a great measure decomposed. The salts of bioxide of palladium are scarcely known.

Ammoniacal compounds of palladium.—A moderately concentrated solution of protochloride of palladium treated with a slight excess of ammonia, yields a beautiful flesh-coloured or rose-coloured precipitate, consisting of NH_3PdCl. This precipitate dissolves in a larger excess of ammonia; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in

the moist state to 212°, or in the dry state to 392°. The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. For this reason, Hugo Müller, who has lately made the ammoniacal compounds of palladium the subject of an elaborate examination, regards the red compound as *ammonio-palladous chloride*, $NH_3 . PdCl$, and the yellow, as *chloride of palladammonium*, $N\overbrace{H_3Pd} . Cl$. The yellow compound, digested with water and oxide of silver, yields the *oxide of palladammonium* (or *palladamine*), $NH_3Pd.O$. This compound is a strong base, analogous to *oxide of platammonium* (p. 374). It is soluble in water, to which it communicates a strong alkaline taste and reaction; by evaporating the solution in vacuo, the base is obtained in the form of a crystalline mass, which absorbs carbonic acid rapidly from the air, especially when moist. It unites with acids, forming definite salts. Its solution precipitates the salts of silver and copper, and an excess of it does not redissolve the precipitates. *Sulphite of palladammonium*, $N\overbrace{H_3Pd} . SO_3$, is formed by saturating the solution of the oxide with sulphurous acid, or by the action of that acid on the yellow chlorine-compound: it crystallises in orange-yellow octohedrons. The *sulphate*, $N\overbrace{H_3Pd} . SO_4$, crystallises in a similar manner. The nitrate, iodide, and bromide have also been formed. The *fluoride* is obtained by adding the chloride to a solution of fluoride of silver.

Chloride of ammopalladammonium (or *chloride of palladdiamine*, according to Müller),

$$2NH_3 . PdCl = N\overbrace{H_2 (NH_4) Pd} . Cl,$$

separates from the ammoniacal solution of chloride of palladammonium, in colourless, oblique rhombic prisms, which

at 392° give off half their ammonia and are reduced to $NH_3Pd . Cl$. The *iodide* and *bromide* of ammopalladammonium are likewise obtained by treating the solutions of iodide and bromide of palladium or palladammonium with ammonia. They both crystallise readily. The *fluoride* is obtained by adding ammonia to the solution of chloride of palladammonium in fluoride of silver, and evaporating: it forms oblique rhombic prisms. The *silico-fluoride* is obtained in crystalline scales on adding hydrofluosilicie acid to any soluble salt of ammopalladammonium. *Oxide of ammopalladammonium*, $\overbrace{NH_3Pd} . O$.—By decomposing the solution of the chloride with oxide of silver,—or better, the sulphate with hydrate of baryta, a strongly alkaline solution is obtained, which, on evaporation, leaves the hydrated oxide in the form of a crystalline mass, though not quite pure. The solution precipitates the salts of aluminium, iron, cobalt, nickel, and copper, but not those of silver; expels ammonia from chloride of ammonium, on boiling; and absorbs carbonic acid from the air. The *carbonate* obtained in this manner, or by decomposing the chloride with carbonate of silver, or the sulphate with carbonate of baryta, crystallises in shining, colourless prisms, which turn yellow a little above 212°; the solution is strongly alkaline, and gives copious precipitates with salts of lime, baryta, copper, and silver. The *sulphite*, $\overbrace{NH_2(NH_4)Pd} . SO_3$, obtained by direct combination, or by the action of ammonia on sulphite of palladammonium, forms small prismatic crystals, sparingly soluble in water, insoluble in alcohol, and turning yellow at about 392°. The *sulphate* obtained by treating palladous sulphate with excess of ammonia, forms small colourless prisms, easily soluble in water, but insoluble in alcohol (Hugo Müller).*

* Ann. Ch. Pharm. lxxxvi. 341.

ESTIMATION AND SEPARATION OF PALLADIUM.

Palladium is always estimated in the metallic state. It is precipitated from its solutions in the form of cyanide by means of a solution of cyanide of mercury, the liquid not containing any excess of acid. The precipitated cyanide of palladium is then reduced to the metallic state by calcination.

Palladium may be separated from nearly all other metals either by precipitation as cyanide, or by precipitation with hydrosulphuric acid, or by the solubility of its oxide in ammonia. But to separate it from copper, with which it is associated in platinum ore, the two metals are precipitated together by hydrosulphuric acid, and the precipitate, while still moist, roasted, together with the filter, as long as sulphurous acid continues to escape. The metals are thereby converted into basic sulphates, which must be dissolved in hydrochloric acid, the solution mixed with nitric acid and chloride of potassium, and evaporated to dryness. A dark saline mass is thus obtained, consisting of chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium; and on treating this mass with alcohol of sp. gr. 0·833, the two former salts are dissolved, and the double chloride of palladium and potassium remains.

SECTION III.

IRIDIUM.

Eq. 98·68, *or* 1233·5; Ir.

The black scales which remain when native platinum is dissolved in aqua-regia, were discovered by Mr. Smithson Tennant to contain iridium and osmium.* The same alloy

* Phil. Trans. 1804.

occurs in flat white metallic grains in native platinum. Iridium has also been observed in combination with about 20 per cent. of platinum, crystallised in octohedrons, which are whiter than platinum, and are said to have a greater density, namely 22·66.

The separation of the osmium and iridium is effected by the following methods: — 1. The osmide of iridium is mixed with an equal weight of common salt, and subjected to the action of a stream of chlorine in a porcelain tube heated to redness. Double chlorides of iridium and sodium, and of osmium and sodium, are then formed; and if the chlorine is moist, a certain quantity of osmic acid, which volatilises, and may be condensed in aqueous ammonia. The mixture of the double chlorides is detached from the tube and boiled with nitric acid. Osmic acid is then evolved, and may be condensed in an alkaline solution, while the chloride of sodium and iridium remains in the solution, and, when mixed with sal-ammoniac, yields a precipitate of chloride of iridium and ammonium, which, on ignition, leaves pure metallic iridium (Wöhler).—2. A mixture of 100 grammes of osmide of iridium and 300 grammes of nitre is placed in an earthen crucible, and heated to bright redness for an hour, the resulting mixture of osmiate and iridiate of potash poured out on a cold metal plate, then introduced into a tubulated retort, and distilled with a large excess of nitric acid. A large quantity of osmic acid then volatilises and condenses in the receiver in beautiful white crystals. As soon as the evolution of osmic acid ceases, water is added, and the residue, consisting of oxide of iridium, with a certain quantity of oxide of osmium, is collected on a filter and boiled with aqua-regia, which dissolves the two metals as chlorides. The solution is then mixed with sal-ammoniac, which precipitates chloride of osmium and ammonium, and bichloride of iridium and ammonium; and the mixed precipitate suspended in water and exposed to a current of sulphurous acid, whereby the compound

$IrCl_2.NH_4Cl$, is converted into $IrCl.NH_4Cl$, which dissolves, while the chloride of osmium and ammonium remains unaltered and does not dissolve: this latter chloride yields pure metallic osmium by calcination. The solution of protochloride of iridium and ammonium leaves, when evaporated, beautiful brown crystals, which yield metallic iridium by calcination.

Iridium is obtained immediately from the chloride, by decomposing that salt with hydrogen at a gentle heat, or by exposing it alone to a very high temperature, in the form of a grey metallic powder, much resembling spongy platinum; also, as above described, from the chloride of iridium and ammonium. It is one of the most refractory bodies known, not being fused by the oxyhydrogen blowpipe. Mr. Children, however, succeeded in fusing a portion of iridium into a globule, by the discharge of a very large voltaic battery. This globule was white and very brilliant, but still a little porous; its density was 18·68. Iridium is neither ductile nor malleable; but it may be obtained in the form of a compact mass, very hard, and capable of taking a good polish, by moistening the pulverulent metal with a small quantity of water, compressing it lightly at first with filtering paper, afterwards very forcibly in a press, and calcining it at a strong white heat in a forge fire. The metal thus aggregated is very porous, and its density does not exceed 16·0. Iridium becomes white and brilliant by strong ignition, without fusion, and is afterwards insoluble in acids. If reduced by hydrogen at a low temperature, it oxidates slowly when heated to redness, or when digested in aqua-regia. This metal is generally rendered soluble by one or other of the following operations. It is calcined with hydrate of potash or nitre, or with a mixture of these salts, which gives a compound of sesquioxide of iridium and potassium. Or, the metal is reduced to a fine powder, and intimately mixed with an equal weight of chloride of potassium or sodium, and the mixture heated to low redness in a stream of chlorine gas. The metal then

combines with chlorine, and the double chloride of iridium and potassium or sodium is formed, which is soluble in water.

Oxides of iridium.—Iridium forms four compounds with oxygen, which are obtained by decomposing the corresponding chlorides. The *protoxide of iridium*, IrO, is obtained from the chloride produced when iridium is heated in chlorine gas; also by precipitating the double chloride of iridium and potassium (KCl . IrCl) with carbonate of potash. The hydrate is then obtained of a greenish grey colour, which is soluble in an excess of the alkaline carbonate. This oxide is the base of a class of salts. The *sesquioxide of iridium*, Ir_2O_3, is formed when the metal is calcined with hydrate of potash or nitre. Berzelius recommends as the best process for procuring it, to mix the double bichloride of iridium and potassium ($KCl + IrCl_2$) with twice its weight of carbonate of potash, and expose it to a low red heat. On dissolving out the alkaline salt, the sesquioxide remains as a very fine powder, of a black colour with a shade of blue. A heat above the melting point of silver is required to expel the oxygen from this oxide. It is reduced to the metallic state by hydrogen gas at the usual temperature, an effect which appears to arise from the oxide of iridium having the property, as well as the metal, to determine the oxidation of hydrogen, a reaction which causes the oxide to be heated to the temperature at which it is itself reduced by hydrogen. The hydrate of this oxide dissolves in acids and forms a particular class of salts, the solutions of which are sometimes of a very dark colour, resembling a mixture of water and venous blood.

Bioxide of iridium, or Iridic oxide, IrO_2.—A solution of sesquichloride of iridium mixed with potash yields no precipitate at first; but if the liquid be heated out of contact with the air, it quickly assumes an indigo colour, absorbs oxygen from the air, and deposits hydrated iridic oxide, $IrO_2 . 2HO$, which may be rendered anhydrous by calcination. This oxide is likewise obtained by dissolving the hydrated sesquioxide in

potash, and treating the solution with an acid. A greenish-blue precipitate is then formed, which gradually absorbs oxygen from the air, and assumes an indigo colour (Claus). This oxide forms salts whose solutions are of a dark, brown-red colour and almost opaque when concentrated, but reddish-yellow when dilute. *Hydrosulphuric acid* decolorises the solutions at first, and afterwards forms a brown precipitate; *hydrosulphate of ammonia* also forms a brown precipitate. *Potash* and *ammonia* decolorise the solution, and produce only a slight black precipitate; but the liquid, on exposure to the air, soon acquires a very fine blue colour. *Carbonate of potash* forms a red-brown precipitate, which gradually dissolves, the liquid afterwards turning blue when exposed to the air. *Carbonate of ammonia* imparts a blue colour to the liquid under the influence of the air. *Chloride of ammonium* forms a dark, cherry-red pulverulent precipitate of bichloride of iridium and ammonium. *Ferrocyanide of potassium* and *protosulphate of iron* decolorise the solution. *Protochloride of tin* forms a light brown precipitate. *Zinc* precipitates metallic iridium as a black powder.

Teroxide of iridium, IrO_3, is formed in small quantity when the alloy of osmium and iridium fused in nitre is digested in aqua-regia. The double terchloride of iridium and potassium then formed yields a rose-red solution, which, when treated with an alkali, slowly deposits the teroxide as a greenish-yellow precipitate, retaining, however, a certain quantity of the alkali. The salts of the protoxide and teroxide afford blue and purple solutions when mixed, depending probably on the formation of one or more combinations of these oxides. The name iridium (from Iris) was applied to this metal, from the variety of colours which its preparations exhibit.

Sulphides of iridium, corresponding with the oxides of the same metal, have been formed.

Chlorides of iridium.—The *protochloride*, $IrCl$, is formed

when iridium in powder is heated to low redness in chlorine gas. As thus prepared, it is insoluble in water, but slightly soluble in hydrochloric acid. It forms double salts with the chlorides of potassium, ammonium, and sodium.

The *sesquichloride*, Ir_2Cl_3, is prepared by dissolving the sesquioxide in hydrochloric acid. It is black, deliquescent, and does not crystallise. It forms soluble double chlorides, which are decomposed by ebullition into iridous double chlorides (containing IrCl), which remain in solution, and iridic double chlorides (containing $IrCl_2$), which are precipitated. Claus has obtained the compounds, $3KCl \cdot Ir_2Cl_3 + 6HO$; $3NH_4Cl \cdot Ir_2Cl_3 + 3HO$; and $3NaCl \cdot Ir_2Cl_3 + 24HO$.

The *bichloride*, $IrCl_2$, is obtained by dissolving very finely-divided iridium, or one of its oxides, in aqua-regia, the liquid being heated to the boiling point. It dissolves in water, forming a reddish-yellow solution. It combines with other chlorides, forming very definite salts. The potassium-salt, *chloridiate of potassium*, $IrCl_2 \cdot KCl \cdot HO$, crystallises in black octohedrons, yielding a red powder, and soluble in water, to which it imparts a red colour. *Chloridiate of ammonium*, $IrCl_2 \cdot NH_4Cl \cdot HO$, is obtained, on mixing the solutions of the two chlorides, as a very dark brown precipitate, which dissolves in boiling water, and crystallises in octohedrons on cooling. Its colouring power is very great, 1 part of it sufficing to impart a distinct coloration to 40,000 parts of water. The red colour often exhibited by chloroplatinate of ammonium is due to traces of this salt. Chloridiate of ammonium dissolves in sulphurous acid, and is thereby converted in a soluble and crystallisable compound of NH_4Cl, and IrCl; the separation of iridium and osmium depends upon this property. Bichloride of iridium, free or combined with other chlorides, is also reduced to the state of protochloride by potash, hydrosulphuric acid, ferrocyanide of potassium, and alcohol. According to Claus,* the bichloride is converted

* Liebig and Kopp's Jähresbericht, 1855, p. 427.

by potash into the olive-green sesquichloride, hypochlorite of potash being formed at the same time. The alkaline solution when heated becomes colourless, and afterwards violet-red, and yields a blue precipitate of the hydrated bioxide; the decolorised alkaline solution, mixed with a few drops of alcohol and heated, deposits metallic iridium. Nitrate of silver added to the solution of the bichloride forms a blue precipitate, which quickly loses its colour and passes into the compound $Ir_2Cl_3 . 3AgCl$. Mercurous nitrate forms a light ochre-yellow precipitate of $Ir_2Cl_3 . 3Hg_2Cl$.

Terchloride of iridium, $IrCl_3$, is formed by treating an oxide or a lower chloride of iridium with very strong aqua-regia, at a temperature not exceeding 104° or 122° (40° or 50° C). Its colour is a deep brown, nearly approaching to black; it is soluble in water, and deliquescent. It forms double chlorides with the chlorides of the alkali-metals.

Carburet of iridium.—When a coherent mass of iridium is held in the flame of a spirit lamp, black masses appear on its surface, which are a carburet, containing 19·83 per cent. of carbon, or IrC_4. The carbon burns off readily in the air.

Iridic sulphate is obtained by dissolving bisulphide of iridium in nitric acid and expelling the excess of acid by evaporation. It dissolves in water and alcohol, forming orange-yellow solutions, which on evaporation leave the salt in the form of a syrupy uncrystallisable mass.

AMMONIACAL COMPOUNDS OF IRIDIUM.—*Ammonio-iridious chloride*, $NH_3 . IrCl$, or *Chloride of iridammonium*, $\overset{\frown}{NH_3Ir} . Cl$. —Prepared by heating bichloride of iridium till it is converted into protochloride, dissolving the brown resinous residue in carbonate of ammonia, and adding hydrochloric acid in slight excess. The compound then separates in the form of a yellow granular precipitate, insoluble in water. The oxide corresponding to this chloride has not been obtained in the free state. The *sulphate* $\overset{\frown}{NH_3Ir} . SO_4$ is obtained by heating the chloride

with dilute sulphuric acid. It crystallises in large orange-yellow laminæ, easily soluble in water. *Biammonio-iridious chloride*, $2NH_3 . IrCl$, or *Chloride of ammiridammonium*, $\overbrace{NH_2(NH_4)Ir} . Cl$, is obtained, as a white precipitate, by boiling the compound, $NH_3Ir . Cl$, with excess of ammonia. Treated with moderately strong sulphuric acid, it yields the corresponding sulphate, $\overbrace{NH_2(NH_4)Ir} . SO_4$, in rhombic prisms; and, by decomposing this salt with nitrate of baryta, or decomposing the chloride with nitric acid, the nitrate is obtained in yellow needles, which dissolve readily in water, melt when heated, and then suddenly decompose with flame. A *chloronitrate of ammiridammonium*, $\overbrace{NH_2(NH_4)Ir} . \left\{\begin{matrix}NO_6\\ Cl\end{matrix}\right.$, or *nitrate of ammochloriridammonium*, $\overbrace{NH_2(NH_4)(IrCl)} . NO_6$, analogous to Gros's platinum-nitrate (p. 379), is obtained as a yellowish, crystalline, granular mass, by heating the chloride of iridammonium, $NH_3Ir . Cl$, with strong nitric acid; when recrystallised from water, it forms shining yellow, laminar crystals. *Bichloride of ammiridammonium*, $\overbrace{NH_2(NH_4)Ir} . Cl_2$, or *chloride of ammo-chloriridammonium*, $\overbrace{NH_2(NH_4)(IrCl)} . Cl$, is obtained by treating the last-mentioned salt with hydrochloric acid, in the form of a violet precipitate, which dissolves readily in hot water, and separates from the solution in violet crystals. Nitrate of silver added to the solution throws down only half the chlorine. The nitrate, treated with dilute sulphuric acid, yields the chlorosulphate of ammiridammonium in delicate greenish, needle-shaped crystals (Skoblikoff).

The compound $5NH_3 . IrCl_3$, or $\left.\begin{matrix}\overbrace{NH_2(NH_4)Ir}\\ \overbrace{NH(NH_4)_2Ir}\end{matrix}\right\} Cl_3$, is obtained by mixing a dilute solution of $Ir_2Cl_3 + 3NH_4Cl$, mixed with excess of ammonia, and leaving the mixture in a well-closed and completely filled bottle for some weeks in a warm place; heating the liquid, which has then acquired a rose-

colour, to expel the excess of ammonia; neutralising with hydrochloric acid; evaporating to dryness; and treating the greenish yellow residue with cold water to extract the chloride of ammonium. A light flesh-coloured, finely crystalline powder then remains, which, when dissolved in boiling water, acidulated with hydrochloric acid, yields, on cooling, a crystalline precipitate of $5NH_3 . Ir_2Cl_3$ mixed with sesquichloride of iridium. This compound when dissolved in a boiling solution of ammonia, is partially decomposed, with separation of blue hydrated bioxide of iridium; when digested with water and oxide of silver, it yields a rose-coloured alkaline solution of the base $5NH_3 . Ir_2O_3$. This solution, saturated with various acids, yields:—the *carbonate*, $5NH_3 . Ir_2O_3 . 3CO_2+3HO$, in the form of a finely crystalline powder, having a light flesh-colour and alkaline reaction; the *nitrate*, $5NH_3 . Ir_2O_3 . 3NO_5$, in indistinct, light flesh-coloured, neutral prisms; and the *sulphate*, $5NH_3 . Ir_2O_3 . 3SO_4$, as a neutral crystalline salt of similar colour. All these salts are soluble in water (Claus).

ESTIMATION AND SEPARATION OF IRIDIUM.

The quantitative estimation of iridium is effected in the same manner as that of platinum, viz. by precipitating with sal-ammoniac and igniting the precipitate. The same method serves to separate iridium from all the preceding metals except platinum. The separation of these two metals is effected by the method already described for the preparation of pure platinum (p. 336); viz. by precipitating with chloride of potassium, fusing the precipitate with carbonate of potash, and dissolving out the platinum with aqua-regia.

SECTION IV.

OSMIUM.

Eq. 99·56 *or* 1244·5 ; Os.

In the treatment of the alloy of iridium and osmium, the latter is separated as a volatile oxide, or osmic acid (p. 394). To obtain the metal, a solution of osmic acid is mixed with hydrochloric acid, and digested with mercury in a well closed bottle at a temperature of 104° (40° Cent.). The osmium is reduced by the mercury, and an amalgam formed, which is distilled in a retort, through which a stream of hydrogen is passed, till all the mercury and calomel formed are removed: osmium then remains as a black powder without metallic lustre. Metallic osmium is also obtained by igniting the sesquichloride of osmium and ammonium mixed with sal-ammoniac.

When rendered coherent, osmium is a white metal, less brilliant than platinum, and very easily pulverised. Its density is about 10. As obtained from the amalgam, osmium is highly combustible; when a mass of it is ignited at a point, it continues to redden, and burns without residue, being converted into the volatile oxide or osmic acid. Osmium in the same condition is oxidated by nitric acid or aqua-regia, and the osmic acid formed distills over with the water and acid. But after being exposed to a red heat, osmium becomes much less combustible in air, and is not oxidated by the humid way, resembling silicon and titanium in that respect. Six different oxides of this metal have been obtained, namely, OsO; Os_2O_3; OsO_2; OsO_3; OsO_4; and OsO_5. The three lowest of these oxides are analogous in composition to the oxides of iridium.

Chlorides and oxides of osmium.—When osmium is heated in a long glass tube by a spirit lamp, and chlorine gas passed

over it, two chlorides are formed, which condense separately in the tube, owing to a difference in their volatility. The *protochloride*, OsCl, which is the least volatile, crystallises in needles of a deep green colour. It is deliquescent, and forms a green solution remarkable for its beauty. This solution is instantly discoloured by great dilution, metallic osmium being deposited, and hydrochloric and osmic acids remaining in solution. Chloride of osmium combines with alkaline chlorides, and acquires greater stability. The *protoxide*, OsO, is obtained by adding potash to a solution of protochloride of osmium and potassium; after some hours, a deep green, almost black, powder is precipitated, which is the hydrated oxide. This hydrate contains alkali. It dissolves slowly but completely in acids, and gives solutions of a deep green colour.

Sesquioxide of osmium, Os_2O_3, is not known in the separate state; but when a mixture of osmic acid and ammonia is kept for some hours at a temperature of 100° to 120°, nitrogen gas is evolved, and a black substance is deposited, containing the sesquioxide in combination with ammonia. It dissolves slowly in acids, and forms yellowish brown solutions, which become brown-black when they contain much oxide. The metal is not precipitated from these solutions by zinc or iron. The corresponding *sesquichloride of osmium* is obtained in combination with chloride of potassium as a double salt, when the preceding oxide containing ammonia is dissolved in hydrochloric acid, and evaporated to dryness; the compound is not crystalline.

Bichloride of osmium, $OsCl_2$, is the more volatile chloride produced when osmium is heated in chlorine. It condenses as a dark red floury powder. Exposed to air, it attracts a little moisture, and forms dendritic crystals. It is soluble in a small quantity of water, giving a yellow solution, but is decomposed by a large quantity, like the protochloride. The bichloride of osmium and potassium is prepared in the same manner as the corresponding salt of iridium. In powder, it

is of a red colour like minium, but forms also the usual octohedral crystals, $KCl . OsCl_2$, which are brown. A solution of this double salt, mixed with carbonate of potash or soda, affords after a time, or immediately, if heated, the corresponding *bioxide of osmium* or *osmic oxide*, OsO_2, as a brown powder, which appears black when collected. This oxide, like the peroxide of iridium, is reduced by hydrogen at ordinary temperatures. It is a base capable of uniting with acids at the moment of its formation.

Osmic sulphate is obtained by treating one of the sulphides of osmium with nitric acid; when dried as completely as possible, it forms a dark yellowish brown syrup, which dissolves in water. The reactions of osmic salts (*e. g.* of the bichloride of osmium and potassium) in solution, are as follows:— *Potash* forms a black precipitate, slowly in the cold, immediately on boiling; *ammonia*, a brown precipitate, after some time; *carbonate of potash*, the same; *chloride of ammonium*, a red precipitate; *protochloride of tin*, a brown precipitate; *mercurous nitrate*, yellowish white; *nitrate of silver*, dark olive-green; *hydrosulphuric acid*, a yellowish brown precipitate after some time; *hydrosulphate of ammonia*, a yellowish brown precipitate insoluble in excess. No precipitate is formed by oxalic acid, ferrocyanide or ferricyanide of potassium, or ferrous sulphate. *Zinc* throws down part of the osmium in the metallic state. *Iodide of potassium* does not form any precipitate, but imparts a deep purple-red colour, which does not disappear when the liquid is heated. *Tannic acid* imparts a deep blue colour.

Osmious acid, OsO_3.—This acid is not known in the separate state, being resolved at the moment of separation from its combinations, into osmic acid and osmic oxide, $2OsO_3 = OsO_4 + OsO_2$. *Osmite of potash*, $KO . OsO_3 + 2HO$, is obtained by the action of reducing agents on the osmiate; thus, when a few drops of alcohol are added to a solution of osmiate of potash, the osmite is precipitated in the

form of a rose-coloured crystalline powder, a strong odour of aldehyde being at the same time evolved, due to the oxidation of the alcohol. Osmite of potash may be obtained in octohedral crystals of considerable size, by mixing a solution of osmiate with nitrite of potash, and leaving the mixture to evaporate slowly. The salt is likewise obtained by dissolving osmic oxide in osmiate of potash. It is rose-coloured, soluble in water, insoluble in alcohol and ether, permanent in dry air, but changes into osmiate under the influence of air and water. Chlorine converts it into osmic oxide and osmiate of potash. It is decomposed by acids, even by the weakest, osmic oxide being precipitated and osmic acid evolved. Sulphurous acid introduced into a solution of this salt, previously rendered alkaline, throws down a yellow crystalline precipitate, containing a salt whose acid is formed of osmium, oxygen, and sulphur. Chloride of ammonium decomposes osmite of potash, forming a nearly insoluble yellow salt, $NH_4Cl \cdot OsO_2NH_2$, which may be regarded as a compound of sal-ammoniac with *osmiamide*, OsO_2NH_2. This compound, heated in a stream of hydrogen, gives off ammonia and sal-ammoniac, and leaves metallic osmium. *Osmite of soda* is prepared in the same manner as osmite of potash, but does not crystallise so easily; its solutions are rose-coloured. Osmious acid does not combine with ammonia; the osmites of potash and soda are rapidly reduced by ammonia.

A *terchloride of osmium* has been obtained in combination with chloride of ammonium, as a double salt, when osmic acid is saturated with ammonia, and treated after a while with excess of hydrochloric acid, mercury being also placed in contact with it. After a few days, the liquid loses the odour of osmic acid, and when evaporated to dryness, leaves the double salt in brown dendritic crystals.

Osmic acid, OsO_4, or the volatile oxide of osmium, is best obtained by the combustion of osmium in a glass tube through which a stream of oxygen gas is passed; it is also obtained

by the action of nitric acid on osmium, and in the decomposition of osmites or osmates by acids. It condenses in long, colourless, regular prismatic needles. The odour of this compound is extremely acid and penetrating, resembling that of the chloride of sulphur. It was from this property of its acid, which is so constantly observed when the oxidable compounds of osmium are heated in air, that osmium obtained its name (from ὀσμος, odour). Its taste is acrid and burning, but not acid. It becomes soft like wax by the heat of the hand, melts into a colourless liquid like water considerably below 212°, and enters into ebullition a very little above its point of fusion. It is dissolved slowly, but in considerable quantity, by water. The solution has no acid reaction. Osmic acid is also soluble in alcohol and ether, but these solutions are apt to deposit metallic osmium. It is a weak acid, being incapable of displacing carbonic acid from the carbonates, in the humid way, but forms a class of salts, the osmiates. Osmic acid is expelled by heat from most of its combinations with bases.

An acid containing more oxygen than osmic acid, and apparently having the formula OsO_5, is formed by submitting the osmiates to the action of oxygen and oxidising agents. It is very unstable; its potash and soda-salts have a dark brown colour, and sometimes crystallise in the alkaline liquids. If the formula OsO_5 be correct, the oxidation-series of osmium will present remarkable analogies with those of nitrogen, phosphorus, and arsenic (Fremy).

Osmiamic acid, Os_2NO_5.—Formed by the action of ammonia on osmic acid, $2OsO_4 + NH_3 . Os_2NO_5 + 3HO$. Its potash-salt is obtained by adding ammonia to a hot solution of osmic acid in excess of potash; the deep orange colour of the liquid soon changes to light yellow, and osmiamate of potash separates in the form of a yellow crystalline powder. The osmiamates of the alkalies and alkaline earths and the zinc-salt are soluble in water; the lead, mercury, and silver-salts insoluble. The aqueous acid is obtained by decomposing

the baryta-salt with sulphuric, or the silver-salt with hydrochloric acid. It may be kept for some days when dilute, but soon decomposes in the concentrated state. It is a powerful acid, decomposing not only the carbonates, but even chloride of potassium. Fritzsche and Struve,* who discovered this acid, assign to it the formula Os_2NO_4, regarding it as a compound of nitride of osmium with osmic acid; $OsN . OsO_4$. Gerhardt, on the contrary,† assigns to it the formula above given, viz., Os_2NO_5, which is the more probable of the two, inasmuch as, if Fritzsche and Struve's were correct, the formation of the acid must be attended with the evolution of 1 eq. oxygen; but they particularly observe that no escape of gas takes place.

Sulphides of osmium.—Osmium has a great affinity for sulphur, and burns in its vapour. Five sulphides of osmium are known, corresponding to all the oxides except the highest, viz., OsS, Os_2S_3, OsS_2, OsS_3, OsS_4. The first four of these sulphides are obtained by decomposing the corresponding chlorides with hydrosulphuric acid. The tetrasulphide is prepared by passing hydrosulphuric acid gas into a solution of osmic acid: it is a sulphur-acid, completely insoluble in water; whereas the others are sulphur bases, slightly soluble in water, and forming deep yellow solutions.

ESTIMATION AND SEPARATION OF OSMIUM.

Osmium is generally estimated in the metallic state. The best mode of separating it from the metals with which it is usually accompanied, is to volatilise it in the form of osmic acid—by distillation with aqua-regia, if the compound be perfectly soluble therein, or by roasting in a stream of oxygen—receiving the vapours of osmic acid in a strong solution of

* J. pr. Chem. xli. 97.

† Compt. rend. de Trans. en Chimie, 1847, 304.

potash; and to reduce this salt, by the addition of a few drops of alcohol, to osmite of potash, which is insoluble in the alcoholic liquor. The osmite of potash is then digested in a cold solution of sal-ammoniac, whereby the compound $NH_4Cl \cdot OsO_2NH_2$ is produced, and the osmium reduced to the metallic state by igniting this last-mentioned compound in a current of hydrogen gas (Fremy).

Another mode of proceeding is to condense the acid vapours evolved by distilling a compound of osmium with aqua-regia in a well-cooled receiver, and precipitate the osmium from the solution by metallic mercury. A precipitate is thereby obtained consisting of calomel, a pulverulent amalgam of osmium, and metallic mercury containing a very small quantity of osmium. This mixture is heated in a glass bulb, through which a stream of hydrogen is passed, whereupon the mercury and its chloride volatilise, and metallic osmium is left in the form of a black powder. The liquid, however, still retains a small quantity of osmium, which may be isolated by saturating the liquid with ammonia, evaporating to dryness, and calcining the residue (Berzelius). The osmium may also be precipitated from the distilled liquid by hydrosulphuric acid, the solution, after complete saturation, being left for several days in a stoppered bottle, till the sulphide of osmium is completely deposited. The sulphide is then washed, dried, and weighed; but as it is apt to retain moisture, and, moreover, oxidises to a certain extent in the air, the method is not very exact. It is recommended, however, for the estimation of small quantities of osmium, the method of precipitating by mercury being better adapted for larger quantities (Berzelius).

SECTION V.

RHODIUM.

Eq. 52 *or* 651·4; R.

This metal was discovered, by Wollaston, in the ore of platinum. He found the ore from Brazil to contain 0·4 per cent; native platinum from another locality has been found with as much as 3 per cent. of rhodium.

After the precipitation of the palladium from the solution of native platinum, by cyanide of mercury, the solution, in order to obtain the rhodium, may be mixed with carbonate of soda and excess of hydrochloric acid, and evaporated to dryness. The cyanide of mercury in excess is decomposed by the hydrochloric acid, and converted into chloride of mercury. The dried mass is reduced to a very fine powder, and washed with alcohol of density 0·837, which takes up the double chlorides of sodium with platinum and iridium, the copper and the mercury, but leaves the double chloride of rhodium and sodium in the form of a fine deep red powder. The rhodium is most easily reduced by gently heating the double chloride in a stream of hydrogen gas, and afterwards washing out the chloride of sodium by water.

Rhodium, when rendered coherent, is a white metal like platinum; its density is about 10·6. It is brittle and very hard, and may be reduced to powder. When pure, it is not dissolved by any acid; but when alloyed with certain metals, such as platinum, copper, bismuth, or lead, and exposed to aqua-regia, it dissolves along with those metals. When fused with gold or silver, however, it is not dissolved with the other metal. But the most eligible mode of rendering rhodium soluble, is to mix it in fine powder with chloride of potassium or sodium, and to heat the mixture to low redness in a stream of chlorine gas. A double chloride is then formed, as with

the other platinum metals in similar circumstances, which is very soluble in water. The solutions of rhodium have a beautiful red colour, the circumstance from which the metal derives its name (from ῥόδον, a rose). Rhodium may also be rendered soluble in the dry way, by fusing it with bisulphate of potash, when the metal is oxidated with escape of sulphurous acid gas. Rhodium is the most oxidable of the platinum metals, combining with oxygen when heated to redness in an open vessel, and very readily when in fine powder and heated to a cherry-red heat. It appears to form two oxides, the rhodous and the rhodic, of which, however, the last only has been completely isolated.

Oxides of rhodium.—The *protoxide* or *rhodous oxide*, RO, is formed when rhodium is ignited in contact with the air. One hundred parts of rhodium thus treated quickly increase to 115·3 parts, corresponding to the protoxide; then slowly, if the ignition be continued, to 118·07 parts; a black powder being formed, consisting of $3RO \cdot R_2O_3$ (Berzelius).

Rhodic oxide, R_2O_3, is produced when the metal is ignited with hydrate of potash and a little nitre, in a silver crucible. The metal swells up, assumes a coffee-brown colour, and is converted into a compound of rhodic oxide and potash, which must be washed with water, and afterwards digested in hydrochloric acid; the hydrated oxide remains of a grey colour, with a shade of green, and insoluble in acids. The same hydrated oxide, as obtained from the double chloride of rhodium and potassium or sodium, by precipitation with an alkali and evaporation, dissolves slowly in acids, together with a certain quantity of alkali which is attached to it, assuming a yellow colour, and producing double salts. The solution in hydrochloric acid is also pale, although it contains chloride of potassium, while a solution of the double chloride, prepared in the way formerly mentioned, has a fine red colour. Hence Berzelius infers that there are two isomeric modifications of this oxide, whose compounds, when in solution, are

respectively yellow and rose-coloured. Hydrated rhodic oxide contains one atom of water, $R_2O_3 . HO$. Two compounds of rhodic oxide with the protoxide of the same metal appear to exist: $R_2O_3 . 3RO$, and $R_2O_3 . 2RO$. The known compounds of rhodium are not isomorphous with compounds of platinum; but this may arise from these two metals affecting combination in different proportions, so that their compounds are not analogous in composition. Their association and resemblance in other respects afford a strong presumption of their being isomorphous bodies.

Solutions of rhodic salts yield, with *hydrosulphuric acid*, a brown precipitate of protosulphide, which is slowly deposited; with *hydrosulphate of ammonia* a brown precipitate, insoluble in excess; with *sulphurous acid* and *sulphites*, a pale yellow precipitate; with *potash*, a yellow precipitate of hydrated rhodic oxide, soluble in excess; with *ammonia*, a yellow precipitate of rhodate of ammonia, which, however, does not form immediately; with *alkaline carbonates*, a yellow precipitate after a while. *Iodide of potassium* produces a slight yellow precipitate; *protochloride of tin* imparts a dark colour to the solutions, but forms no precipitate. Acetate of *lead*, *mercurous* nitrate, and nitrate of *silver* form precipitates analogous in composition to the iridium-salts already mentioned (p. 397). *Zinc* precipitates metallic rhodium. In a solution of rhodium mixed with excess of potash, *alcohol* forms, even at ordinary temperatures, a black precipitate, probably consisting of metallic rhodium; with the other platinum-metals, this reaction takes place only when the liquid is heated. No precipitate is formed by phosphate of soda, sal-ammoniac, chloride of potassium, chromate of potash, oxalic acid, cyanide of potassium, cyanide of mercury, ferrocyanide or ferricyanide of potassium, or gallic acid. *Hydrogen gas* reduces the anhydrous salts at a moderate heat.

Sulphide of rhodium.— Rhodium may be united with sulphur by either the dry or the humid way. The sulphide of

rhodium was used by Wollaston to obtain the metal in a coherent mass.

Protochloride of rhodium, RCl, is obtained by heating the protosulphate (precipitated from rhodic salts by hydrosulphuric acid) in a stream of chlorine; or by digesting one of the intermediate oxides with hydrochloric acid, whereupon the sesquichloride dissolves, and the protochloride remains in the form of a reddish grey powder insoluble in water.

Sesquichloride of rhodium, R_2Cl_3, is obtained from the double chloride of rhodium and potassium, by precipitating the latter metal with fluosilicic acid. The dry salt thus obtained is brown black, and not crystalline; it requires a pretty high temperature to decompose it, and then resolves itself at once into chlorine and rhodium. This salt deliquesces in air; its solution in water is of a beautiful red colour (Berzelius). Sesquichloride of rhodium is also obtained in the form of a rose-red powder by heating the metal to low redness in a stream of chlorine (Claus). This red powder, which was regarded by Berzelius as $R_2Cl_3 . 2RCl$, is slowly decomposed when heated in hydrogen gas, is insoluble in strong hydrochloric and aqua-regia even at the boiling heat, is coloured yellow by continued boiling with potash, and if afterwards boiled with strong hydrochloric acid, dissolves in small quantity, forming a rose-coloured solution, the greater part, however, remaining unaltered.

A *chloride of rhodium and potassium*, containing $2KCl . R_2Cl_3 + 2HO$, is obtained by the action of chlorine on a mixture of rhodium and chloride of potassium, or by evaporating a solution of the sesquichloride of rhodium and sodium with chloride of potassium. It forms brown, doubly oblique prisms, which dissolve sparingly in water. Another double salt, containing $3KCl . R_2Cl_3 + 6HO$, is obtained in dark red, sparingly soluble, efflorescent prisms, by spontaneous evaporation of a solution of the hydrated sesquioxide in hydrochloric acid mixed with chloride of potassium. The *sodium double-salt*,

$3NaCl \cdot R_2Cl_3 + 24HO$, forms doubly oblique prisms of a deep cherry-red colour. With *chloride of ammonium*, two double salts are obtained, viz., $2NH_4Cl \cdot R_2Cl_3 + 2HO$, and $3NH_4Cl \cdot R_2Cl_3 + 3HO$, both of which form red prismatic crystals. By precipitating either of the above double chlorides containing 2 or 3 eq. of the basic chloride to 1 eq. R_2Cl_3, with acetate of *lead, mercurous* nitrate, or nitrate of *silver*, rose-coloured precipitates are formed, containing 2 or 3 eq. of $PbCl$, Hg_2Cl, or $AgCl$, to 1 eq. of R_2Cl_3 (Claus).

A *sulphate of rhodium* is formed when rhodium is ignited with bisulphate of potash; it gives a yellow solution. Another sulphate in combination with sulphate of potash gradually falls as a white powder, when sulphuric acid is added to a solution of the double chloride of these bases. It is nearly insoluble in water; its formula is $KO \cdot SO_3 + {}_2O_3 \cdot 3SO_3$. *Nitrate of rhodium* is formed by dissolving the oxide in nitric acid. It forms a deliquescent salt of a dark red colour, $R_2O_3 \cdot 3NO_5$; the last salt combines with nitrate of soda, forming dark red crystals soluble in water but not in alcohol: $NaO \cdot NO_5 + R_2O_3 \cdot 3NO_5$.

The salts of rhodium are often mixed with peculiar rose-coloured salts, whose nature is not exactly known. These new salts are not precipitated, either by iodide of potassium in the cold, or by sulphurous acid, or by ammonia; they form, with chloride of ammonium, double salts, which crystallise, not in scales, but in red prisms (Fremy).

ESTIMATION AND SEPARATION OF RHODIUM.

Rhodium is estimated in the metallic state. The solution containing it is mixed with excess of carbonate of soda and evaporated to dryness, the residue ignited, and the calcined mass treated with cold water: oxide of rhodium then remains, and may be reduced by hydrogen.

Rhodium is separated from many metals with which it may be alloyed, by fusing the alloy with bisulphate of potash; the rhodium is thereby converted into sulphate of rhodium and potassium, which may be dissolved out by water. The method of separating it from platinum and the allied metals has already been given.

The separation of rhodium from other metals in solution is somewhat difficult, because it is not completely precipitated by hydrosulphuric acid. To separate rhodium from *copper*, the solution is saturated with hydrosulphuric acid and left to stand in a stoppered bottle for twelve hours, then filtered, and the filtrate heated to separate an additional portion of sulphide of rhodium. The whole of the precipitate is then roasted in a platinum crucible till the sulphides are completely oxidised, and the product treated with strong hydrochloric acid, which dissolves the copper and leaves the oxide of rhodium. The liquid filtered from the hydrosulphuric acid precipitate still contains a small portion of rhodium, which may be precipitated by carbonate of soda and converted into oxide as above. The whole of the oxide is then reduced by hydrogen.

To separate rhodium from *iron*, the rhodium is precipitated as completely as possible by hydrosulphuric acid; the liquid filtered; and the iron in the filtrate precipitated by ammonia, after having been brought to the state of sesquioxide. The iron-precipitate carries down with it a certain portion of rhodium, which may be separated by igniting the precipitate in a current of hydrogen, and treating the reduced metals with hydrochloric acid, which dissolves the iron and leaves the rhodium: the latter is then converted into oxide by ignition in the air. The precipitated sulphide of rhodium is likewise oxidised by roasting. The small quantity of rhodium which remains in solution after precipitation by ammonia is precipitated by carbonate of soda, and converted into oxide by ignition. The whole of the oxide of rhodium is then reduced to the metallic state by hydrogen.

The separation of rhodium from the alkali-metals is easily effected by converting the metals into chlorides, and igniting the chlorides in a current of hydrogen, which reduces only the chloride of rhodium.

SECTION VI.

RUTHENIUM.

Eq. 52·1 *or* 651·25; Ru.

This metal was discovered by Claus in 1846. It occurs in platinum ores, chiefly in the native osmide of iridium, which contains from 3 to 6 per cent. of it. To separate it, the osmide of iridium is pulverised, mixed with about half its weight of common salt, and heated to low redness in a current of moist chlorine gas. The disintegrated mass is then digested in cold water, and the concentrated solution, which is brown-red and almost opaque, mixed with a few drops of ammonia and gently heated, whereupon it deposits a copious black-brown precipitate, consisting of sesquioxide of ruthenium and bioxide of osmium. This precipitate, after being washed with nitric acid, is heated in a retort, till the osmium is expelled in the form of osmic acid. The residue is then ignited for an hour in a silver crucible with caustic potash free from silica, and the ignited mass softened and dissolved by cold distilled water. The solution is left in a corked bottle for two hours to clarify; after which the perfectly transparent orange-coloured liquid is separated by a siphon, and neutralised with nitric acid. It then deposits velvet-black sesquioxide of ruthenium, which, when washed, dried, and ignited in an atmosphere of hydrogen, yields the pure metal.

Ruthenium is a grey metal, very much like iridium. Its

specific gravity is 8·6.* It is very brittle, does not fuse even in the flame of the oxy-hydrogen blowpipe, and is scarcely attacked by aqua-regia. It combines with oxygen in four proportions, forming the three oxides, RuO, Ru_2O_3, RuO_2, and ruthenic acid, RuO_3. Its affinity for oxygen is greater than that of any of the other platinum metals, except osmium. When heated to redness in the air, it oxidises readily, forming a bluish black oxide, which does not part with its oxygen at a white heat. When fused with nitre or with caustic potash, it is converted into rutheniate of potash. It is not dissolved by fused bisulphate of potash.

Protoxide of ruthenium, RuO.—Obtained by igniting the protochloride with carbonate of soda, in a stream of carbonic acid gas, and washing the residue with water. It is a blackish grey powder, containing 13·4 per cent. of oxygen. It is insoluble in acids, and consequently its salts have not been directly formed.

The *protochloride*, $RuCl$, is obtained in the anhydrous state, by heating the metal to low redness in a stream of chlorine. It is a black crystalline substance, insoluble in water and acids, and imperfectly decomposed by alkalies. A soluble protochloride appears, however, to be formed by passing hydrosulphuric acid gas through a solution of the sesquichloride.

Sesquioxide of ruthenium, Ru_2O_3.—Pulverulent ruthenium, strongly heated before a powerful blowpipe turns black, and rapidly absorbs oxygen, 100 parts of the metal increasing to 118 parts; afterwards the oxidation slowly proceeds further till the oxide acquires a blackish blue colour, and contains 23 or 24 parts of oxygen to 100 parts of metal, which is about the proportion required for the sesquioxide. The *hydrated*

* This is much less than the density usually attributed to iridium (p. 395.). It is probable, however, that the two metals do not really differ much in density; for a specimen of porous iridium prepared from the blue oxide, by reduction with hydrogen, exhibited a density of only 9·3 (Claus).

sesquioxide is formed by precipitating a solution of the sesquichloride with an alkali, by decomposing a solution of rutheniate of potash with nitric acid, or by heating the aqueous solution of the sesquichloride. It is a black-brown powder, which becomes suddenly incandescent when heated. Hydrogen gas reduces it imperfectly at ordinary temperatures. It is insoluble in alkalies, but dissolves in acids, forming orange-yellow solutions. The solution in hydrochloric acid exhibits the following reactions:—*Hydrosulphuric acid* partly precipitates the ruthenium in the form of a black sulphide, but at the same time reduces the sesquichloride to protochloride, the reduction being attended with a change of colour from orange-yellow to a fine azure blue: this reaction is extremely delicate, and very characteristic of ruthenium. *Zinc* effects the same reduction. *Hydrosulphate of ammonia* throws down the greater part of the ruthenium in the form of a black-brown sulphide, not perceptibly soluble in excess. The *caustic alkalies, alkaline carbonates,* and *phosphate of soda* precipitate the black sesquioxide, insoluble in excess of the reagent. *Borax* forms no precipitate at first, but, on heating the solution, the hydrated sesquioxide is thrown down. *Sulphurous acid, oxalic acid,* and *formiate of soda* do not precipitate the metal, but merely decolorise the solution. *Ferrocyanide of potassium* decolorises the solution at first, but afterwards turns it bluish green. Acetate of *lead* forms a purple-red precipitate, inclining to black. *Cyanide of mercury* colours the solution blue, and throws down a blue precipitate. Nitrate of *silver* forms a black precipitate, which is a mixture of chloride of silver and sesquioxide of ruthenium; the oxide dissolves, after a while, in the nitric acid, leaving a white residue of chloride of silver; and, if ammonia be then added in excess, the chloride of silver dissolves, and the sesquioxide of ruthenium is reprecipitated: this is also a very delicate reaction. The *chlorides of potassium* and *ammonium* throw down from concentrated solutions, crystalline precipitates

of double chlorides, exhibiting a play of colours inclining to violet.

Sesquichloride of ruthenium, Ru_2Cl_3, is obtained in the solid state by evaporating the solution of the sesquioxide in hydrochloric acid. The residue is deliquescent, has a very astringent but not metallic taste, and dissolves in water and alcohol, forming beautiful orange-coloured solutions, but leaving a yellow basic compound undissolved. When heated, it turns green and blue. The dilute solution is resolved by heat into hydrochloric acid and the hydrated sesquioxide (pp. 414, 415). The sesquichloride forms double salts with the chlorides of potassium and ammonium, and apparently also with those of sodium and barium.

Bioxide of ruthenium, Ruthenic oxide, RuO_2, is formed by roasting and igniting the bisulphide, or by strongly igniting the sulphate, $RuO_2 . 2SO_3$; the former method yields a black-blue powder, with a tinge of green; the latter, grey particles with metallic lustre and bluish or greenish iridescence. The *hydrate*, $RuO_2 . 2HO$, is obtained as a gelatinous precipitate by decomposing the bichloride of ruthenium and potassium with carbonate of soda. The precipitate, when dried and heated in a platinum spoon, deflagrates with vivid incandescence, and is scattered about. It dissolves in acids, forming solutions which are yellow when dilute and rose-coloured when concentrated.

The *bichloride* is not known in the separate state, but forms with chloride of potassium a double salt, $KCl,RuCl_2$, which is obtained by treating the sesquichloride of ruthenium and potassium with aqua-regia. This double salt is very soluble in water, but insoluble in alcohol; its colour is brown inclining to rose-red. The aqueous solution has a deep rose-colour, strongly resembling that of sesquichloride of rhodium. Hydrosulphuric acid acts but slowly on this solution, producing first a milky turbidity from precipitated sulphur, and afterwards throwing down a yellowish brown sulphide; the

solution, however, still retains a deep rose-colour and does not turn blue.

Ruthenic sulphate, $RuO_2 . 2SO_3$.—When the sulphide obtained by treating the sesquichloride with hydrosulphuric acid is digested in moderately strong nitric acid, an orange-yellow solution is formed, which, on evaporation, yields this salt in the form of a yellowish brown amorphous mass. It is deliquescent, and dissolves readily in water. Alkalies added to the solution form no precipitate at first; but, on evaporating, a yellowish brown gelatinous precipitate is obtained, consisting of hydrated ruthenic oxide, and strongly resembling impure rhodic oxide. The solution of this salt does not turn blue when treated with hydrosulphuric acid.

Ruthenic acid, RuO_3, is known only in the form of a potash-salt, which is obtained by igniting ruthenium with a mixture of potash and nitrate or chlorate of potash. It dissolves in water, forming an orange-yellow solution, which has an astringent taste, colours organic substances black by coating them with oxide, and is decomposed by acids, yielding a precipitate of the sesquioxide.

Sulphides of ruthenium.—This metal probably forms with sulphur a series of compounds analogous to the oxides; but it is difficult to obtain them in a definite state. Sulphur and ruthenium do not combine directly, and the precipitates thrown down by hydrosulphuric acid from the chlorides always contain excess of sulphur. When the sulphide obtained by precipitation from the sesquichloride is heated in an atmosphere of carbonic acid, incandescence and explosion take place, sulphur and water pass off, and a blackish grey metallic powder is left, whose analysis agrees with the formula Ru_2S_3. All the sulphides are dissolved by nitric acid of ordinary strength (Claus).

ESTIMATION AND SEPARATION OF RUTHENIUM.

This metal is precipitated from its solutions in the form of oxide, and generally as sesquioxide, viz. from a solution of the sesquichloride, either by alkalies or by simply heating the solution, and from a solution of rutheniate of potash by nitric acid. The precipitated oxide is reduced to the metallic state by ignition in an atmosphere of hydrogen. As, however, the precipitate generally contains alkali, which cannot be removed by washing, the reduced mass must be treated with water; the liquid filtered from the ruthenium; and the metal, before weighing, must be again ignited and left to cool in an atmosphere of hydrogen, as it oxidises when heated in the air. Ruthenium has hitherto been found only associated with the metals of the platinum-residues, and from these it is separated by the method described at page 413., depending on the resolution of the aqueous sesquichloride by heat into hydrochloric acid and sesquioxide of ruthenium.

NEW METHOD OF TREATING PLATINUM-RESIDUES.*

When platinum-ore has been exhausted by aqua-regia, a residue is left, commonly known by the name of *osmide of iridium.* This residue is a mixture of two different substances, one of which is scaly, and consists of osmium, iridium, and ruthenium; while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium. Now oxide of ruthenium can bear a red heat without decomposing, and osmium is actually roasted by the action of oxygen, producing a volatile acid, just as sulphur and arsenic do; hence the residue of platinum-ore may be decomposed by roasting; and by submitting it to

* Fremy, Compt. rend. xxxviii. 1008; also Traité de Chimie Générale, par Pelouze et Fremy, iii 452.

this operation, osmic acid is produced in large quantity and very pure, and oxide of ruthenium is obtained in well-defined crystals. The roasting is performed as follows :—

About 200 grammes of platinum-residue (the sealy and granular alloys together) are heated to bright redness in a porcelain tube placed in a long furnace. Air is drawn through the tube by means of an aspirator, being first made to pass through solution of potash to free it from carbonic acid, and through strong sulphuric acid to remove organic matter. The air thus purified passes over the heated platinum-residue, and forms osmic acid and oxide of ruthenium. The latter crystallises in the colder parts of the roasting tube, while the more volatile osmic acid is carried forward, first into a series of empty tubes, in which part of it settles in the form of crystals, and then through two bottles filled with solution of potash, which retains the uncondensed vapours: the apparatus terminates with an aspirator. The products of the operation are:—1. Oxide of ruthenium, in violet crystals, the form of which is similar to that of native oxide of iron; 2. Osmic acid, very pure, and sometimes amounting to 40 per cent. of the platinum-residue used; 3. Osmiate of potash, which, by the addition of a few drops of alcohol, may be converted into osmite of potash, a salt from which metallic osmium may be obtained (p. 403); 4. An alloy of iridium and rhodium, which remains in the roasting tube.

This last residue may be used for the preparation of iridium and rhodium. For this purpose, it is calcined in an earthen crucible with four times its weight of nitre, care being taken not to carry the process too far; and the residue is exhausted with boiling water and filtered. A copious precipitate is thereby formed, which remains on the filter, and the filtrate consists of an alkaline liquid, which, when left to evaporate, deposits crystals of osmite of potash, the osmium never being completely removed by the previous roasting.

The precipitate which remains on the filter and retains a

considerable quantity of potash, is subjected to the action of aqua-regia, which converts the iridium into chloriridiate of potassium, nearly insoluble in cold water: the action of the aqua-regia must be continued for several hours. The mass is then treated with boiling water, which dissolves the chlor-iridiate of potassium, the washing being continued till the extract no longer exhibits a brown colour. The solutions are then evaporated, and the chloriridiate of potassium obtained in crystals.

The undissolved portion, which contains the rhodium, is dried, mixed with an equal weight of chloride of sodium, and subjected for three or four hours to the action of dry chlorine at a dull red heat. Chlororhodiate of sodium is thereby formed, and may be obtained, by solution in water and evaporation, in beautiful rose-coloured octohedral crystals, resembling chrome-alum.

Rhodium is likewise obtained in another stage of the treatment of platinum-ore. When this ore is treated with aqua-regia a certain quantity of rhodium is dissolved together with the platinum, although rhodium by itself is insoluble in aqua-regia. The solution is evaporated to dryness, the residue dissolved in water, and the solution mixed with sal-ammoniac to precipitate the platinum. The rhodium then remains in solution, together with a small quantity of platinum, to separate which a plate of iron is immersed in the liquid, and the pulverulent mixture of platinum and rhodium thereby precipitated is digested in weak aqua-regia, which dissolves the platinum and leaves the rhodium nearly pure. From this residue, pure well-defined crystals of chlororhodiate of sodium may be obtained in the manner just described (Fremy).

SUPPLEMENT.

HEAT.

EXPANSION OF SOLIDS.

The following determinations of the amount of the cubical expansion of solids for each degree Centigrade, at temperatures not exceeding 100° C., are given by H. Kopp*, the volume of the solid at 0° being taken equal to 1:—

Table I.—Cubical Expansion of Solids.

Substance.	Formula.	Cubical Exp. for 1° C.	Substance.	Formula.	Cubical Exp. for 1° C.
Copper	Cu	0·000051	Arragonite	$CaO.CO_2$	0·000065
Lead	Pb	0·000089	Calcspar	$CaO.CO_2$	0·000018
Tin	Sn	0·000069	Bitterspar	$CaO.CO_2 + MgO.CO_2$	0·000035
Iron	Fe	0·000037	Iron-spar	$Fe(Mn, Mg)O.CO^2$	0·000035
Zinc	Zn	0·000089	Heavy spar	$BaO.SO_3$	0·000058
Cadmium	Cd	0·000094	Cœlestin	$SrO.SO_3$	0·000061
Bismuth	Bi	0·000040	Quartz	SiO_3	0·000042 0·000039
Antimony	Sb	0·000033	Orthoclase	$KO.SiO_3 + Al_2O_3.3SiO_3$	0·000026 0·000017
Sulphur	S	0·000183	Soft soda glass	. . .	0·000026
Galena	PbS	0·000068	Another sort	. . .	0·000024
Zinc-blende	ZnS	0·000036	Hard potash glass	. . .	0·000021
Iron pyrites	FeS_2	0·000034			
Rutile	TiO_2	0·000032			
Tin stone	SnO_2	0·000016			
Iron-glance	Fe_2O_3	0·000040			
Magnetic iron ore	Fe_3O_4	0·000029			
Fluor-spar	CaF	0·000062			

* Ann. Ch. Pharm. lxxxi. 1.

The mode of experimenting consisted in taking the specific gravity of the solid substance at a lower and at a higher temperature, by ascertaining the quantity of water together with a known weight of the solid substance, and also the quantity of water alone, which filled a vessel of constant capacity at the different temperatures. The determinations in the instances of iron and glass, and the second determinations of quartz and orthoclase, were made with mercury instead of water, and calculated in a similar manner.

Kopp has also determined the expansion of some other solids, especially near the melting points.* Most bodies, at temperatures near their melting points, exhibit a sudden increase in the rate of expansion. The increase of volume which a substance exhibits in the fused state, as compared with the same substance at lower temperatures, arises, partly from the great expansion which it undergoes as it approaches the melting point, partly from the sudden expansion which takes place in fusing. In some substances, however, only one of these modes of expansion is at all considerable.

Phosphorus (the yellow modification), of sp. gr. 1·826 at 10° C. (50° F.), expands uniformly up to its melting point 44° C. (111·2° F.), at which temperature its volume is 1·017 of the volume at 0° C.; but, at the moment of fusion, it exhibits a sudden expansion amounting to 3·4 per cent., so that its liquid volume at 44° C. is 1·052.

Sulphur (native crystals, sp. gr. 2·069) expands irregularly near its melting point (115° C. or 239° F.). Its volume being 1 at 0° C., is 1·010 at 50° C. (122° F.); 1·037 at 100° C.; 1·096 at 115° C.; at the moment of fusion, the expansion amounts to 5 per cent., the volume then increasing to 1·150.

Wax (bleached beeswax, sp. gr. 0·976 at 10° C.) expands very rapidly as it approaches its melting point (64° C. or

* Ann. Ch. Pharm. xciii. 129.

147·2° F.), but only 0·4 per cent. more at the moment of fusion. If the volume at 0° C. is 1, the volume at 50° C. (122° F.) is 1·068; at 60° C. (14·0° F.) is 1·128; at 64° C. (147·2° F.) is 1·161, and increases by fusion to 1·166.

Water expands at the moment of freezing by about 10 per cent. 1·1 volume of ice gives 1 volume of water at 0° C., which, when heated to 4° C. (39·2° F.), contracts to 0·99988, but expands progressively at higher temperatures, its volume at 100° being 1·043.

Solid hydrated salts, on the contrary, expand at the moment of fusion; *e. g.* chloride of calcium ($CaCl + 6HO$), by 9·6 per cent.; ordinary phosphate of soda ($2NaO.HO.PO_5 + 24HO$) and hyposulphite of soda ($NaOS_2O_2 + 5HO$), each by 5·1 per cent.

Rose's fusible metal (2 parts bismuth, 1 part tin, and 1 part lead, sp. gr. 8·906 at 10° C.) expands, when heated from 0° to 59° C. (32° to 138·2° F.), in the ratio of 1 to 1·0027; but contracts when further heated, its volume at 82° C. (179·6° F.) being equal to that at 0° C., and at 95° C. (203° F.) equal to 0·9947; in fusing, between 95° and 98° C., it expands by 1·55 per cent., so that at 98° C. (208·4° F.) its volume is equal to 1·0101. This alloy, therefore, contracts from 59° C. up to its melting point.

EXPANSION OF LIQUIDS.

M. Pierre's researches on this subject have been continued.* The expansions of a great number of liquids have also been determined by H. Kopp.†

* Annales de Chimie et de Physique, [3], xxi. 118, xxxiii. 119.

† Pogg. Ann. lxxii. 1 and 223; and Ann. Ch. Pharm. xciii. 157; xciv. 257; xcv. 307; xcviii. 367.

Pierre concludes from his experiments that isomeric liquids in general do not contract equally at an equal number of degrees below their respective boiling points; an exception is, however, presented by acetate of methyl ($C_2H_3O . C_4H_3O_3$) and formiate of ethyl ($C_4H_5O . C_2HO_3$), in which the contraction for equal intervals below the boiling points appears to be equal.*

Table II. exhibits the contractions of several groups of isomeric liquids, at D° centigrade below the boiling point, as determined by Pierre and by Kopp.

TABLE II. — EXPANSION OF LIQUIDS.

D.	Aldehyde, $C_4H_4O_2$.		Butyric Acid, $C_8H_8O_4$.		Acetate of Ethyl, $C_8H_8O_4$.		D.
	Pierre (B. P. 22°).	Kopp (20·8°).	Pierre (163°).	Kopp (157°).	Pierre (74·1°).	Kopp (74·3°).	
0	10000	10000	10000	10000	10000	10000	0
10	9817	9830	9872	9867	9846	9843	10
25	9567	9596	9688	9677	9629	9622	25
45	9284	. .	9453	9439	9359	9352	45
60	9094	. .	9288	9271	9172	9165	60
75	. .	. .	9128	9112	8996	8988	75
110	. .	. .	8781	8765	8633	. .	110

D.	Chloride of Ethylene, $C_4H_4Cl_2$ Pierre (84·9°).	Monochlorinated Chloride of Ethyl, $C_4H_4Cl_2$. Pierre (64·8°).	Monochlorinated Chloride of Ethylene, $C_4H_3Cl_3$. Pierre (114·2°).	Bichlorinated Chloride of Ethyl, $C_4H_3Cl_3$. Pierre (74·9°).	Formiate of Ethyl, $C_6H_6O_4$.		Acetate of Methyl, $C_6H_6O_4$.		D.
					Pierre (52·9°).	Kopp (54·9°).	Pierre (59·5°).	Kopp (56·3°).	
0	10000	10000	10000	10000	10000	10000	10000	10000	0
25	9677	9669	9693	9648	9632	9631	9633	9631	25
55	9331	9300	9350	9267	9241	9243	9243	9243	55
80	9068	9003	9090	8988	8953	. .	8955	. .	80

* The contrary statement originally made by Pierre, and quoted at p. 7. Vol. I. of this work, was founded on an error of calculation.

Expansion of water. — Table III. contains the results obtained by Kopp*, and also those of Pierre as calculated by Frankenheim †, with regard to the expansion of water between 0° and 100° C., the volume at zero being taken as the unit.

TABLE III. — EXPANSION OF WATER.

Temp.	Volume.		Temp.	Volume.	
	Kopp.	Pierre.		Kopp.	Pierre.
–15° C.	. .	1·003758	19°	1·001370	
–10	. .	1·001658	20	1·001567	1·001594
– 5	. .	1·000582	21	1·001776	
0	1·000000	1·000000	22	1·001995	
1	0·999947		23	1·002225	
2	0·999908		24	1·002465	
3	0·999885		25	1 002715	1·002708
4	0·999877		30	1·004064	1·004071
5	0·999883	0·999890	35	1·005697	1·005677
6	0·999903		40	1·007531	1·007512
7	0·999938		45	1·009541	1·009563
8	0·999986		50	1·011766	1 011815
9	1·000048		55	1·014100	1·014360
10	1·000124	1·000148	60	1·016590	1·017118
11	1·000213		65	1·019302	1·019947
12	1·000314		70	1·022246	1·022938
13	1·000429		75	1·025440	1·026078
14	1·000556		80	1·028581	1·029360
15	1·000695	1·000728	85	1·031894	1·032769
16	1·000846		90	1·035397	1·036294
17	1·001010		95	1·039094	1·039925
18	1·001184		100	1·042986	1·043649

The maximum density Frankenheim finds, from the same data, to exist at the temperature of 3·86° C. or 38·95° F.; Playfair and Joule ‡ fix the point of maximum density at 3·945° C. or 39·1° F.; Plücker and Gessler §, at 3·8° C. or 38·8° F.

* Pogg. Ann. lxxii. 223.
† Pogg. Ann. lxxxvi. 451.
‡ Phil. Mag. [3], xxx. 41.
§ Pogg. Ann. lxxxv. 238.

Absolute expansion of mercury. — From numerous measurements of the pressures exerted by columns of mercury of equal height but different temperatures, Regnault* finds that if the volume of mercury at 0° C. be = 1, the volume at $t°$ of the air-thermometer is given by the formula —

$$1 + 0{\cdot}000179007t + 0{\cdot}0000000252316\, t^2.$$

Hence, the values in

TABLE IV. — EXPANSION OF MERCURY.

Temp.	Volume.	Temp.	Volume.
50°	1·009013	250°	1·046329
100	1·018153	300	1·055973
150	1·027419	350	1·065743
200	1·036811		

Militzer has also determined the absolute expansion of mercury by similar means, but only at ordinary temperatures, the temperature of the colder column of mercury ranging, in his experiments, between 2° and 4° C., and that of the warmer column between 19° and 23°. The mean coefficient of expansion for 1°, deduced from these experiments, is $0{\cdot}00017405 \pm 0{\cdot}00000082$.† The experiments of Dulong and Petit (i. 8.) give for 1° the coefficient 0·00018018.

* "Rélations des Expériences entreprises, pour determiner les principales lois physiques et les données numériques qui entrent dans le calcul des machines à vapeur." Paris, 1847.

† Pogg. Ann. lxxx 55.

SPECIFIC HEAT.

The specific heat of most bodies is greater in the liquid than in the solid state. The following determinations are by Regnault: —

TABLE V. — SPECIFIC HEAT.

Substance.	Solid.		Liquid.	
	Temperature.	Sp. Heat.	Temperature.	Sp. Heat.
Lead . . .	0° to 100° C.	0·0314	350° to 450° C.	0·0402
Bromine . .	−78 „ −20	0·08432	10 „ 48	0·1109
Iodine . .	0 „ 100	0·05412	. .	0·10822
Mercury . .	−78 „ −40	0·0247	0 „ 100	0·0333
Sulphur . .	0 „ 100	0·2026	120 „ 150	0·234
Bismuth . .	0 „ 100	0·03084	280 „ 380	0·0363
Zinc . . .	0 „ 100	0·0956		
Tin . . .	0 „ 100	0·0562	250 „ 350	0·0637
Phosphorus .	10 „ 30	0·1887	50 „ 100	0·2120
—— Amorphous	15 „ 98	0·1700		
Water . .	below 0	0·502	0 „ 20	1·0000
Crystallised chloride of calcium	below 0	0·345	33 „ 80	0·555
Nitrate of soda .	0 to 100	0·27821	320 „ 430	0·413
Nitrate of potash	0 „ 100	0·23875	350 „ 435	0·3319

Table VI. exhibits the specific heats of several liquids as determined by H. Kopp*, and by Favre and Silbermann.† The second column shows the intervals of temperature in Kopp's determinations. Those of Favre and Silbermann were made by cooling the liquids in a mercurial calorimeter of peculiar construction, from their several boiling points to temperatures nearly equal to that of the surrounding atmosphere.

* Pogg. Ann. lxxv. 98.

† Comptes Rendus, xxiii. 524.

TABLE VI. — SPECIFIC HEAT.

Liquids.	Temperature.	Sp. Heat.	Observers.
Mercury . . .	44° to 24°C.	0.0332	Kopp.
Iodine	. .	0·10822	F. S.
Bromine . . .	45 „ 11	0.107	Andrews.
Sulphuric acid . . .	46 „ 21	0·343	Kopp.
Wood-spirit . . .	43 „ 23	0·645	Kopp.
		0·6713	F. S.
Alcohol . . .	43 „ 23	0·615	Kopp.
		0 6438	F. S.
Fusel-oil . . .	44 „ 26	0·564	Kopp.
		0·5873	„
Ethal	. .	0·5059	F. S.
Ether	. .	0·50342	„
Formic acid . . .	45 „ 24	0·536	Kopp.
Acetic acid . . .	45 „ 24	0·509	„
Butyric acid . . .	45 „ 21	0 503	„
Formiate of ethyl . .	39 „ 20	0·513	„
Acetate of methyl . .	41 „ 21	0·507	„
Acetate of ethyl . .	45 „ 21	0·496	„
		0·48344	F. S.
Butyrate of methyl . .	45 „ 21	0·487	Kopp.
		0·49176	F. S.
Valerate of methyl . .	45 „ 21	0·491	Kopp.
Acetone . . .	41 „ 20	0·530	„
Benzole. . . .	46 „ 19	0·450	„
Oil of mustard . . .	48 „ 28	0·432	„
Oil of turpentine . .	. .	0·46727	F. S.

The specific heat of water at different temperatures has been determined by Regnault*, from whose experiments it appears that the quantity of heat expressed in *heat-units*† which one gramme of water loses in cooling down from $t°$ to 0° C. is given by the formula—

$$Q = t + 0{\cdot}00002\, t^2 + 0{\cdot}0000003\, t^3;$$

and the specific heat C at the temperature $t°$, that is to say, the quantity of heat required to raise one gramme of water from $t°$ to $(t + 1)°$, is—

$$C = 1 + 0{\cdot}00004\, t + 0{\cdot}0000009\, t^2.$$

* "Rélations," &c. (see note, p. 426), 729.

† See page 448.

From this formula, the following numbers are obtained:—

TABLE VII.—SPECIFIC HEAT.

t.	Q.	C.	t.	Q.	C.
0°	0·000	1·0000	150°	151·462	1·0262
50	50·087	1·0042	200	203·200	1·0440
100	100·500	1·0130	230	234·708	0·0568

Specific heat of gases and vapours.—On this subject numerous experiments have been made by Regnault *, who finds, contrary to the statement of Delaroche and Bérard, that the specific heat of a gas does not vary, either with its density or with its temperature. The specific heat of atmospheric air, referred to water as unity, is found to be 0·2377 between − 30° and + 10° C.; it is 0·2379 between 10° and 100°; and 0·2376 between 100° and 225°.

Table VIII. contains Regnault's determinations of the specific heats of a considerable number of gases; in column A, as referred to equal weights (water = 1); in column B, as referred to equal volumes.

TABLE VIII.—SPECIFIC HEAT OF GASES (REGNAULT).

	A.	B.		A.	B.
Oxygen . . .	0·2182	0·2412	Ether . . .	0·4810	1·2296
Nitrogen . . .	0·2440	0·2370	Chloride of ethyl .	0·2737	0·6117
Hydrogen . .	3·4046	0·2356	Bromide of ethyl .	0·1816	0·6717
Chlorine . . .	0·1214	0·2967	Sulphide of ethyl .	0·4005	1·2568
Bromine . . .	0·0552	0·2992	Cyanide of ethyl .	0·4255	0·8293
Nitrous oxide . .	0·2238	0·3413	Chloroform . .	0·1568	0·8310
Nitric oxide . .	0·2315	0·2406	Chloride of ethylene	0·2293	0·7911
Carbonic oxide .	0·2479	0·2399	Acetate of ethyl .	0·4008	1·2184
Carbonic acid . .	5·2164	0·3308	Acetone . . .	0·4125	0·8341
Sulphide of carbon .	0·1575	0·4146	Benzole . . .	0·3754	1·0114
Sulphurous acid .	0·1553	0·3489	Oil of turpentine .	0·5061	2·3776
Hydrochloric acid .	0·1845	0·2302	Terchloride of phosphorus .	0·1346	0·6386
Hydrosulphuric acid	0·2423	0·2886	Chloride of arsenic .	0·1122	0·7013
Ammonia . .	0·5080	0 2994	Chloride of silicon .	0·1329	0·7788
Marsh-gas . .	0·5929	0·3277	Bichloride of tin .	0·0939	0·8639
Olefiant gas . .	0·3694	0·3572	Bichloride of titanium	0·1263	0 8634
Water-vapour . .	0·4750.	0·2950			
Alcohol-vapour .	0·4513	0·7171			

* Compt. Rend. xxxvi. 676.

LIQUEFACTION.

The melting point of a body appears to be influenced to a minute but certain amount, by the pressure to which it is subjected. W. Thomson *, by enclosing transparent pieces of ice and water in an Oersted's water-compressing apparatus, found that the melting point of the ice was lowered 0·059° C. by a pressure of 8·1 atmospheres, and 0·129° by a pressure of 16·8 atmospheres. Bunsen † has obtained similar results with spermaceti and paraffin.

SPERMACETI.

Pressure in Atmospheres.	Solidifying Point.
1	47·7° C.
29	48·3
96	49·7
141	50·5
156	50·9

PARAFFIN.

Pressure in Atmospheres.	Solidifying Point.
1	46·3° C.
85	48·9
100	49·9

Such results are in conformity with the deductions by J. Thomson ‡ from the mechanical theory of heat.

The *latent heat of water* was found by Regnault, and by Provostaye and Desains, to be 79° C. or 142 F. According to Person, this number denotes the quantity of heat required to convert ice at 0° C. into water, but not the total quantity of the latent heat in the water, inasmuch as a certain additional portion of heat is rendered latent as the temperature of the ice rises from −2° to 0°.§ In six experiments on the fusion of ice previously cooled to temperatures between −2° and −21°, the latent heat was found to vary between 79·9 and 80·1, the mean quantity being 80° C., or 144° Fah. Regnault also found greater values for the latent heat of water in proportion

* Phil. Mag. [3], xxxvii. 123.

† Pogg. Ann. lxxxi. 562.

‡ Edinb. Phil. Trans. vol. xvi.

§ Ann. Ch. Phys. [3], xxx. 73.

as the ice used in the experiments had been cooled to a lower temperature. According to Hess, the true latent heat of water is 80·34° C. = 144·6° Fah. For the specific heat of ice, Hess finds the number 0·533; Person finds 0·48 for the temperatures between − 21° and − 2°, the specific heat of water being 1.

Table IX. contains the latent heats of fusion, and the melting points of various solids, as determined by Person.*

TABLE IX. — LATENT HEAT OF FUSION.

Substances.	Melting point.	Latent Heat.
Tin	235° C.	14·3
Bismuth	270	12·4
Lead	332	5·15
Alloy $Pb_2\ Sn_2\ Bi_3$	96	5·96
Alloy $Pb\ Sn_2\ Bi$	145	7·63
Phosphorus	44·2	4 71
Sulphur	115	9·175
Nitrate of Soda	310.5	62·98
Nitrate of Potash	339	46·18
A mixture of 1 eq. Nitrate of Soda and 1 eq. Nitrate of Potash	219·8	51·4
Phosphate of Soda $2NaO,\ HO,\ PO_5 + 24HO$	36·4	66·80
Chloride of Calcium $CaCl,\ 6HO$ . .	28·5	40·70
Bees-wax (yellow)	62·0	43·51
Zinc	423·0	27·46

LATENT HEAT OF VAPOURS.

Water. — It is stated at page 58, vol. i. of this work, that the sum of the latent and sensible heats of steam is the same at all temperatures. This is commonly known as Watt's law. Southern, on the other hand, maintained that the latent heat alone is constant at all temperatures. But the late elaborate researches of Regnault† have shown that both these

* Pogg. Ann. lxx. 300; Ann. Ch. Phys. [3], xxvii. 250.

† "Rélations des Expériences," &c. (see Note, p. 426), 271; also "Works of Cavendish Society," i. 294.

statements are incorrect, and that the total quantity of heat (expressed in heat-units*), which a unit of weight of saturated aqueous vapour contains at the temperature $t°$ centigrade, exceeds the amount contained in the same weight of water at 0°, by the quantity —

$$\lambda = 606{\cdot}5 + 0{\cdot}305\,t.$$

If from this, we subtract the quantity of heat which a unit of weight of water at $t°$ contains, beyond that which is contained in the same weight of water at 0° (see Regnault's determinations of the specific heat of water at different temperatures, p. 428), we shall obtain the latent heat L of the vapour of water at the temperature $t°$. The values of λ and L for various temperatures are given in Table X., together with the tensions expressed in millimetres and in atmospheres.

Table X. — Latent Heat of Steam.

Temperature.	Tension.		λ	L.
	mm.	atm.		
0° C	4·60	0.006	606·5	606·5
50	91·98	0·121	621·7	571·6
100	760·00	1·000	637·0	536·5
150	3581·23	4·712	652·2	500·7
200	11688·96	15·380	667·5	464·3
230	20926·40	27·535	676·6	441·9

The latent heats of the vapours of several other liquids at their boiling points have been determined by Andrews†, and by Favre and Silbermann.‡ The results are given in—

* A unit of heat is the quantity required to raise the temperature of a unit of weight (1 gramme, 1 pound, &c.) of water at 0°, by 1° Centigrade.

† Chem. Soc. Qu. J. i. 27.

‡ Ann. Ch. Phys. [3], xxxvii. 461.

Table XI.—Latent Heat of Vapours.

Substances.	Boiling point.	Latent Heat of Vapour.	Observers.
Water . . .	100° at 760 mm.	535·9	Andrews.
" . . .	100	536	F. and S.
Iodine . . .	. .	23·95	"
Bromine . . .	58 " 760	45·60	A.
Sulphurous acid . .	. .	94·56	F. and S.
Terchloride of phosphorus .	78·5 " 767	51·42	A.
Bichloride of tin . .	112·5 " 752	3·053	"
Bisulphide of carbon .	46·2 " 769	86·67	"
Alcohol . . .	77·9 " 760	202·40	"
" . . .	78·4	208·92	F. S.
Wood-spirit . . .	65·8 " 767	263·70	A.
" . . .	66·5	263·86	F. S.
Fusel-oil . . .	132	121·37	"
Ether . . .	35·6	91·11	"
" . . .	34·9 " 752	90·45	A.
Amylic ether . .	113	69·40	F. S.
Acetic acid . . .	120	101·91	"
Formic acid . . .	100	120·72	"
Valerianic acid . .	175	103·52	"
Butyric acid . .	16.4	114·67	F. S
Acetate of ethyl . .	74	105.80	"
" . .	74·6 " 762	92·68	A.
Acetate of methyl . .	55 " 762	110·20	"
Formiate of ethyl . .	54·3 " 762	105·30	"
Formiate of methyl . .	32·9 " 752	117·10	"
Iodide of ethyl . .	71·3 " 760	46·87	"
Iodide of methyl . .	42·2 " 752	46·07	"
Oxalate of ethyl . .	184·4 " 779	72·72	"
Butyrate of methyl . .	93·0² " 779	87·33	F. S.
Ethal . . .	360·0²	58·48	"
Oil of turpentine . .	156	68·73	"
Terebene . . .	156	67·21	"
Oil of lemons . .	165	70·02	"
Hydrocarbons—			
(*a*) $C_{12}H_{12}$ . . .	198	59·9	"
(*b*) $C_{15}H_{15}$ . . .	255	59·7	"

TENSION OF VAPOURS.

Regnault* has made a vast number of observations on the tension of aqueous vapour in vacuo, between the temperatures of $-32°$ and $+147·5°$ C., and given formulæ of interpolation for calculating the tension at any given temperature between those limits.

* Ann. Ch. Phys. [3], xi. 273

For temperatures between 0° and 100° the interpolation formula is —

$$\log e = a + b\alpha^t + c\beta^t;$$

in which t denotes the temperature, e the tension, and a, b, c, α, β are constants whose values are determined by five equations of condition, obtained by substituting in the preceding equation the corresponding observed values of t and e for the temperatures 0°, 25°, 50°, 75°, and 100°. (See Table, p. 65, vol. i.) The values thus obtained are —

$$\log \alpha = 0{\cdot}006865036 \qquad \log c = 0{\cdot}6116485$$
$$\log \beta = \bar{1}{\cdot}9967249 \qquad a = +\,4{\cdot}7384380.$$
$$\log b = \bar{2}{\cdot}1340339$$

For temperatures below 0°, Regnault adopts the formula —

$$e = a + b\alpha^x;$$

in which —

$$x = t - 32; \ \log b = \bar{1}{\cdot}4724984; \ \log \alpha = 0{\cdot}0371566;$$
$$a = +\,0{\cdot}131765.$$

For temperatures above 100° C. the interpolation formula is —

$$\log e = a - b\alpha^x; \ x = t - 100°;$$

in which —

$$\log \alpha = \bar{1}{\cdot}9977641; \ \log b = 0{\cdot}4692291;$$
$$a = +\,5{\cdot}8267890.$$

It has not yet been found possible to include the whole series of observations in one formula of interpolation.

From the first and second of these formulæ, the following table of tensions* is calculated for every half degree between −10° and +35°. This table (which is the one alluded to in the note at page 94, vol. i.) is of great utility in hygrometric observations: —

* Ann. Ch. Phys. [3], xv. 138.

TABLE XII.

Tension of Aqueous Vapour from $-10°$ *to* $+35°$ C.

Degrees.	Tension.	Diff.	Degrees.	Tension.	Diff.	Degrees.	Tension.	Diff.
	mm.			mm.			mm.	
−10·0	2·078	0·090	+ 5·0	6·534	0·229	+ 20·0	17·391	0·544
9·5	2·168	0·093	5·5	6·763	0·235	20·5	17·935	0·560
9·0	2·261	0·095	6·0	6·998	0·244	21·0	18·495	0·574
8·5	2·356	0·100	6·5	7·242	0·250	21·5	19·069	0·690
8·0	2·456	0·105	7·0	7·492	0·259	22·0	19·659	0·601
7·5	2·561	0·105	7·5	7·751	0·265	22·5	20·265	0·623
7·0	2·666	0·110	8·0	8·017	0·274	23·0	20·888	0·640
6·5	2·776	0·114	8·5	8·291	0·283	23·5	21·528	0·656
6·0	2·890	0·120	9·0	8·574	0·291	24·0	22·184	0·674
5·5	3·010	0·121	9·5	8·865	0·300	24·5	22·858	0·692
5·0	3·131	0·126	10·0	9·165	0·309	25·0	23·550	0·711
4·5	3·257	0·130	10·5	9·474	0·318	25·5	24·261	0·727
4·0	3·387	0·135	11·0	9·792	0·328	26·0	24·988	0·750
3·5	3·522	0·140	11·5	10·120	0·337	26·5	25·738	0·767
3·0	3·662	0·145	12·0	10·457	0·347	27·0	26·505	0·789
2·5	3·807	0·148	12·5	10·804	0·358	27·5	27·294	0·807
2·0	3·955	0·154	13·0	11·162	0·368	28·0	28·101	0·830
1·5	4·109	0·158	13·5	11·530	0·378	28·5	28·931	0·851
1·0	4·267	0·163	14·0	11·908	0·390	29·0	29·782	0·872
0·5	4·430	0·170	14·5	12·298	0·401	29·5	30·654	0·894
0·0	4·600	0·167	15·0	12·699	0·413	30·0	31·548	0·915
+ 0·5	4·767	0·173	15·5	13·112	0·424	30·5	32·463	0·942
1·0	4·940	0·178	16·0	13·536	0·436	31·0	33·405	0·963
1·5	5·118	0·184	16·5	13·972	0·449	31·5	34·368	0·991
2·0	5·302	0·189	17·0	14·421	0·461	32·0	35·359	1·011
2·5	5·491	0·196	17·5	14·882	0·475	32·5	36·370	1·030
3·0	5·687	0·202	18·0	15·357	0·488	33·0	37·410	1·063
3·5	5·889	0·208	18·5	15·845	0·501	33·5	38·473	1·092
4·0	6·097	0·216	19·0	16·346	0·515	34·0	39·565	1·115
4·5	6·313		19·5	16·861		34·5	40·680	1·147
						35·0	41·827	

Regnault has also determined the tensions of several other liquids in vacuo. The results (given in Table XIII.) were obtained either by direct measurement of the elastic forces in vacuo, or by determining the temperature of the vapour of a boiling liquid under the pressure of an artificial atmosphere. The former method was adopted for low, the latter for high temperatures. The series of experiments made by the two methods were, however, in all cases made to include a certain common range of temperature, so that the corresponding

curves of tension might overlap each other within that range. With liquids which could be obtained perfectly pure, such as water and sulphide of carbon, the two curves thus obtained were found to coincide exactly; but with alcohol, ether, and still more with chloroform, which are more difficult to purify, the presence of foreign substances gave rise to more or less divergence in the results. Thus the tension of chloroform vapour at 36°, was found to be 342·2 mm. by the first method, and 313·4 mm. by the second. Regnault finds that an extremely small amount of impurity may be detected in this manner.

Table XIII. — Tension of Vapours.

Temperature.	Alcohol.	Ether.	Sulphide of Carbon.	Chloroform.	Oil of Turpentine.
	mm.	mm.	mm.	mm.	mm.
−21° C.	3·12				
−20	3·34	69·2			
−16	. .	. .	58·8		
−10	6·50	113·2	79·0		
0	12·73	182·3	127·3	. .	2·1
10	24·08	286·5	199·3	130·4	2·3
20	44·00	434·8	298·2	190·2	4·3
30	78·4	637·0	434·6	276·1	7·0
40	134·10	913·6	617·5	364·0	11·2
50	220·3	1268·0	852·7	524·3	17·2
60	350·0	1730·3	1162·6	738·0	26·9
70	539·2	2309·5	1549·0	976·2	41·9
80	812·8	2947·2	2030·5	1367·8	61·2
90	1190·4	3899·0	2623·1	1811·5	91·0
100	1685·0	4920·4	3321·3	2354·6	134·9
110	2351·8	6249·0	4136·3	3020·4	187·3
116	. .	7076·2			
120	3207·8	. .	5121·6	3818·0	257·0
130	4351·2	. .	6260·6	4721·0	347·0
136	. .	. .	7029·2		
140	5637·7	. .	. .	. .	462·3
150	7257·8	. .	. .	. .	604·5
152	7617·3				
160	. .	. .	. .	. .	777·2
170	. .	. .	. .	. .	989·0
180	. .	. .	. .	. .	1225·0
190	. .	. .	. .	. .	1514·7
200	. .	. .	. .	. .	1865·6
210	. .	. .	. .	. .	2251·2
220	. .	. .	. .	. .	2690·3
222	. .	. .	. .	. .	2778·5

Vapours of saline solutions. — It is well known that the boiling point of a saline solution is higher than that of pure water, the affinity of the water for the salt being, in fact, an additional obstacle which the heat must overcome before ebullition can take place. Nevertheless, it appeared to Rudberg that the vapours rising from such solutions do not exhibit a higher temperature than steam from boiling water; a result which was attributed to the sudden expansion which the vapour undergoes at the moment of escaping from the liquid. Regnault finds, however, that a thermometer having its bulb immersed in the vapour of a boiling saline solution does not give a correct indication of the temperature of that vapour, because the bulb becomes covered with a film of condensed water, and, therefore, the thermometer exhibits only the temperature due to the boiling of that water. But when proper precautions are taken, by the interposition of screens, to prevent, as far as possible, this deposition of water, the temperature of the vapour appears very nearly equal to that of the liquid. It is, however, extremely difficult to remove this source of error completely.

The observation of the elastic force of a vapour arising from a saline solution appears to afford excellent means of detecting chemical changes in the constitution of the liquid, every such change being indicated by the occurrence of a *singular point* in the curve which represents the law of the tension. For example, in the case of salts, like the sulphates of sodium, copper, iron, manganese, &c., which crystallise at different temperatures with different proportions of water, Regnault suggests that the variations in the tension of the vapour might indicate whether the water is chemically combined with the salt while still in solution, or whether the combination takes place at the moment of crystallisation.

Mixtures of vapours and gases. — The law of Dalton, that the tension of any saturated vapour in air is the same for

any given temperature as in vacuo, must be received with certain limitations. It has been already stated (i. 91) that Regnault found the tension of saturated aqueous vapour in air to be always somewhat less than in vacuo; the differences, however, seldom exceeding 2 per cent. of the entire value. The following are a few of the results obtained: —

TABLE XIV.

Temperature.	Observed Tension in Air.	Calculated Tension in Vacuo.	Difference.
	mm.	*mm.*	
0° C.	4·47	4·60	−0·13
12·59	10·31	10·85	−0·54
15	12·38	12·70	−0·32
21	18·27	18·49	−0·22
24·69	22·70	23·13	−0·40
31	32·97	33·41	−0·44
35·97	43·39	44·13	−0·74
38	48·70	49·30	−0·60

Similar differences are observed with other liquids. With ether the following results are obtained: —

TABLE XV.

Temperature.	Tension of Ether-vapour.		
	In Air.	In Vacuo.	Difference.
	mm.	*mm.*	*mm.*
33·62° C.	705·09	726·0	20·9
30·97	645·52	659·0	13·4
26·52	552·67	559·2	6·5
22·63	479·63	484·0	4·4
20·05	429·69	433·9	4·2
19·99	428·88	433·0	4·1
14·26	337·71	341·0	3·3

In air and in hydrogen gas, the tension of ether vapour was found to be always lower than in vacuo, unless the gas was strongly compressed; in carbonic acid gas, which (as a liquid)

dissolves ether in considerable quantity, the tension never becomes equal to that in vacuo.

The tension of a vapour in a gas is very much affected by the condensation of the vapour on the sides of the vessel, an effect which takes place considerably below the point of saturation. Regnault is of opinion that Dalton's law with regard to the tensions of vapours in gases could never be strictly true, unless the gas were enclosed in a vessel whose walls were, to a certain thickness, formed of the liquid itself.

Vapours of mixed liquids. — Gay-Lussac found that the tension of the vapour arising from two or more mixed liquids is equal to the sum of the tensions of the vapours which each would produce separately. The more recent experiments of Magnus and of Regnault have shown that this law is true, or nearly true, only when the liquids are quite immiscible, such as benzol and water. When the liquids are mutually soluble, but not in all proportions, the tension of the mixed vapour is much less than the sum of the separate tensions. With ether and water it scarcely differs from the tension of the ether-vapour alone; thus: —

Table XVI.

Temperature.	Tension of water-vapour.	Tension of ether-vapour.	Sum of tensions.	Observed tension of mixed vapour.
	mm.	*mm.*	*mm.*	*mm.*
15·66° C.	13·16	361·8	374·96	362·95
24·21	22·47	510·0	532 47	510·08
33·08	37·58	711·1	748·68	710·02

When the mixed liquids dissolve in one another in all proportions, the tension of the mixed vapour is in most cases greater than that of the less volatile, but less than that of the more volatile substance; such, for example, is the case with mixtures of ether and sulphide of carbon. In a mixture of benzol and alcohol, however, the tension of the mixed vapour

is greater than that of either of the separate vapours. With this mixture Regnault obtained the results given in —

Table XVII.

Temperature.	Tension of vapour.		
	Of the mixture.	Of alcohol.	Of benzol.
7·22° C.	43·17	40·4	20·1
9·98	50·22	46·8	24·2
13·11	59·66	54·4	29·2
16·05	69·43	62·7	35·0
18·59	79·35	71·0	41·0

When the liquids do not mix, but dispose themselves in layers, the more volatile liquid forming the lower stratum, and the ebullition being but feeble, the temperature and corresponding vapour-tension agree with Gay-Lussac's law. But with a brisk fire and violent ebullition, the temperature remains nearly at the limit at which the more volatile liquid would boil by itself under the same pressure.

CONDUCTION OF HEAT.

In metals. — From the experiments of Wiedemann and Franz*, it appears that the metals follow each other with regard to their heat-conducting power, in the same order as with regard to their power of conducting electricity; and, moreover, that the numbers which express their relative heat-conducting powers, do not differ from those which express their relative powers of conducting electricity, more than the latter numbers, as determined by different observers, differ from each other.

The heat-conducting power of metals appears also to diminish as their temperature rises.

* Phil. Mag. [4], vii. 33.

TABLE XVIII.

Metals.	Electric-conducting power according to			Heat-conducting power.
	Riess.	Becquerel.	Lenz.	
Silver . .	100	100	100	100
Copper . .	66·7	91·5	73·3	73·6
Gold . .	59·0	64·9	58·5	53·2
Brass . .	18·4	——	21·5	23·6
Tin . . .	10 0	14·0	22·6	14·5
Iron . . .	12·0	12·35	13·0	11·9
Steel . .	——	——	——	11·6
Lead . .	7·0	8·27	10·7	8·5
Platinum . .	10·5	7·93	10·3	8·4
German silver .	5·9	——	——	6·3
Bismuth . .	——	——	1·9	1·8

Conduction of heat in crystallised bodies.—Bodies of perfectly homogeneous structure conduct heat with equal facility in all directions; so likewise do crystallised bodies belonging to the regular system; but in crystals belonging to any other system, the rate of conduction is different in different directions. This subject has been very ingeniously investigated by Senarmont*, whose method of observation was as follows:—A small tube of platinum was inserted through the centre of a flat cylindrical plate of the crystal in the direction of the axis, the tube being bent at right angles at the lower extremity and heated by a lamp, and a current of air made to pass through the tube by means of an aspirator. The two bases of the cylindrical plate were covered with wax, which, being melted by the heat, traced on the surface a curve line, whose form was determined by the conducting power of the crystal in different directions. Plates of non-crystalline substances, such as glass and zinc, treated in this manner, gave circles having their centres in the axis of the platinum-tube. On a plate of *calc-spar*, cut perpendicularly to the axis of symmetry (the optic axis), the curves are circles with their centres in the axis. On plates parallel to the direction of

* Ann. Ch. Phys. [3], xxi. 45.

natural cleavage, the curves are also circles, having a slight tendency to elongate in the direction of the principal section. On plates cut parallel to the axis of symmetry, and at right angles to one of the faces of the primary rhombohedron, the curves are ellipses, having their transverse diameter in the direction of the axis of symmetry. The ratio of the axes of the ellipse thus formed is 1·118 : 1. Similar results are obtained with quartz, the ratio of the axes being 1·31 : 1; also with crystals belonging to the square prismatic system, such as rutile, idocrase, and subchloride of mercury. In crystals belonging to the right prismatic, oblique prismatic, and doubly oblique prismatic systems, — that is to say, in crystals having two axes of double refraction, — three directions are found at right angles to each other, in which the thermal curves, obtained in the manner above described, are ellipses. Hence it is inferred that: —

1. In crystalline media having two optic axes, supposing the medium to be indefinitely extended in all directions, and a centre of heat to exist within it, the isothermal surfaces are ellipsoids with three unequal axes.

2. In crystals with one optic axis, the isothermal surfaces are ellipsoids of revolution round that axis.

3. In crystals belonging to the regular system, and in homogeneous uncrystallised media, the isothermal surfaces are spherical.

Uncrystallised bodies, however, acquire axes of different heat-conducting power when their molecular structure is altered by pressure, traction, or hardening. Plates of glass subjected to lateral pressure, and heated in the manner above described, exhibit distinct thermic ellipses, having their shorter axes in the direction of the pressure, that is, of the greatest density (Senarmont). It is well known that glass, and other transparent non-crystalline bodies, when similarly treated, acquire the power of double refraction.

Crystalline media likewise exhibit peculiar characters in

the transmission of heat by *radiation* as well as by conduction. Through crystals with one optic axis, heat is radiated in different quantity and also of different quality (i. 37), according as it passes in a direction parallel or perpendicular to that axis. In crystals with two optic axes, the quantity and quality of the transmitted heat differ according as the direction of transmission coincides with one or other of the three axes of elasticity (Knoblauch).*

Conducting power of wood.—The dependence of heat-conduction upon molecular arrangement is exhibited by organic structures as distinctly as by crystalline media. This subject has been very ingeniously investigated by Dr. Tyndall †, who has examined the conducting power of various organic substances, especially of wood. The bodies cut into cubes of equal size, were enclosed between two chambers filled with mercury, that liquid being confined on the sides next the cube by membranous diaphragms, with which the cube was in close contact. The mercury in one of the chambers was heated by a spiral of platinum wire immersed in it, and connected with a galvanic battery. The heat thus generated was transmitted through the organic substance to the mercury in the other chamber, and the quantity of heat thus communicated in a given time, was measured by means of a thermo-electric couple connected with a galvanometer. By transmitting heat in this manner through cubes of wood in different directions, it was found that:

At all points not situated in the centre of the tree, wood possesses three unequal axes of calorific conduction. The first and principal axis is parallel to the fibres of the wood; the second and intermediate axis is perpendicular to the fibres and to the ligneous layers; and the third, and least axis, is perpendicular to the fibre and parallel to the layers.

These axes of heat-conduction coincide with the axes of

* Pogg. Ann. lxxxv. 169; xciv 161.

† Phil. Mag. [4], vi. 121.

elasticity, which Savart discovered by observing the figures of sand formed on plates of wood when thrown into acoustic vibration. The same directions are likewise axes of *cohesion* and of *permeability to liquids.* Wood of any kind may be most easily split by laying the blade of the cutting instrument parallel to the fibres and across the annual rings; the direction of least cohesion is, therefore, perpendicular to the fibres, and parallel or tangential to the rings. The direction of greatest resistance is parallel to the fibres. With regard to permeability, it is well known that plates of wood cut perpendicularly to the fibres are not fit for the bottoms of casks to hold liquids; also, that in cutting staves for casks, it is indispensable to cut them across the woody layers, the direction parallel to the layers being that of least permeability.

It may, therefore, be stated as a general law, that: *the axes of calorific conduction in wood coincide with the axes of elasticity, cohesion and permeability to liquids, the greatest with the greatest, and the least with the least.*

The heat-conducting power of wood does not bear any definite relation to its density. American birch, which is one of the lightest woods, conducts heat better than any other. Oak and Coromandel wood, which are very dense, conduct nearly as well; but iron-wood, which has the enormous density of 1·426, is very low in the scale of conduction.

RELATION BETWEEN HEAT AND MECHANICAL FORCE OR WORK.—DYNAMICAL THEORY OF HEAT.

Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapours evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction shows with equal clearness that motion may be converted into heat. That the rise of

temperature thus produced is not due to any change in the heat-capacity of the bodies, is strikingly shown in Davy's experiment of melting ice by rubbing two plates of the substance together *in vacuo* (i. 101); and Count Rumford's observations on the heat produced by the boring of ordnance point to the same conclusion. In these and all similar cases, the heat appears as a direct result of the force expended: the motion is converted into heat.

But the connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact numerical law, a given quantity of the one being always convertible into a determinate quantity of the other. The first approximate determination of this numerical relation—*the mechanical equivalent of heat*—was made by Count Rumford in the following manner: A brass cylinder, enclosed in a box containing a known weight of water at 60° F., was bored by a steel borer made to revolve by horse-power, and the time noted which elapsed before the water was raised to the boiling-point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water, 1° F., is equivalent to 1034 times the force expended in raising a pound weight one foot high, or to 1034 *foot-pounds*, as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessels, or of that which was lost by dispersion during the progress of the experiment.

For the most exact determinations of the mechanical equivalent of heat, we are indebted to the careful and elaborate experiments of Mr. J. P. Joule. From experiments made in the years 1840-1843, on the relations between the heat and mechanical power generated by the electric current, Mr. Joule was led to conclude that the heat required to raise the temperature of a pound of water 1° F., is equivalent to 838 foot-pounds; and a nearly equal result was

afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too high.

The most trustworthy results are, however, obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases. But, in 1842, Meyer showed that the temperature of water may be raised 22° or 23° F. by agitating it. The warmth of the sea after a few days of stormy weather is also, probably, an effect of fluid friction.

In 1843 Mr. Joule showed that heat is evolved in the passage of water through narrow tubes, and that each degree of heat per pound of water required for its evolution in this way a force of 770 foot-pounds. In subsequent experiments, a paddle-wheel was employed to produce fluid friction, and the equivalents 781·5, 782·1 and 787·6 obtained from the agitation of water, sperm-oil, and mercury respectively.

The apparatus finally employed by Mr. Joule* in the determination of this important constant, by means of the friction of water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 21 shows a vertical and fig. 22 a horizontal section, was firmly fitted into a copper vessel (A, fig. 23) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, and having six rotatory and eight sets of stationary vanes, was used for experiments on the friction of mercury. The apparatus for the friction of solids con-

Fig. 21.

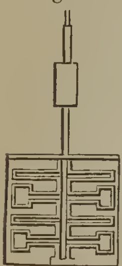
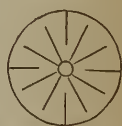


Fig. 21.



* Phil. Trans. 1850, i. 61; Chem. Soc. Qu. J. iii. 316.

sisted of a vertical axis carrying a bevelled cast-iron wheel, against which a fixed bevelled wheel was pressed by a lever. The wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus

Fig. 23.

motion was given to the axis by the descent of leaden weights suspended by strings from the axes of two wooden pulleys *w*, one of which is shown at *p* (fig. 23), their axes being supported on friction-wheels *d d*; and the pulleys were connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

The mode of experimenting was as follows: The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained, after which the roller was set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the

paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the experiments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were capable of indicating a variation of temperature as small as $\frac{1}{200}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method; the second column gives the results as they were obtained in air; the third column, the same results corrected for a vacuum.

Material employed.	Equivalent in air.	Equivalent *in vacuo*.	Mean.
Water . . .	773·640	772·692	772·692
Mercury . .	773·762	772·814	774·083
	776·303	775·352	
Cast-iron . .	776·997	776·045	774·987
	774·880	773·930	

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration of the frame-work of the apparatus and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because, even in the friction of fluids, it is impossible entirely to avoid vibration and sound.

The conclusions deduced from these experiments are—

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of* 1 *lb. of water (weighed in vacuo, and between* 55° *and* 60°) *by* 1° *F., requires for its evolution the expenditure of a mechanical*

force represented by the fall of 772 *lbs. through the space of* 1 *foot.*

Or, the heat capable of increasing the temperature of 1 *gramme of water by* 1° *cent., is equivalent to a force represented by the fall of* 423·55 *grammes through the space of* 1 *metre. This is consequently the effect of a "unit of heat."*

Kupffer* has also determined the mechanical equivalent of heat by comparing the expansion which a metal wire suffers by heat with the elongation produced by stretching it with a given weight. By this method, which does not appear to be quite so accurate as that above described, it is found that the heat necessary to raise a pound of water 1° Fahrenheit, is equivalent to 661 foot-pounds.

DYNAMICAL THEORY OF HEAT.

The constant relation between heat and work affords a powerful argument in favour of the mechanical or dynamical theory of heat—the theory which rests on the hypothesis that HEAT IS MOTION. This theory has received, of late years, many important additions and developments, chiefly by the labours of Clausius, Joule, Rankine, and W. Thompson. It is impossible, within the limits of this Supplement, to give even a brief account of the whole of these valuable researches; but the leading points of the theory may, perhaps, be sufficiently elucidated by the following summary of two remarkable papers lately published in "Poggendorff's Annalen," one by Krönig, entitled "Fundamental Principles of a Theory of Gases;"† the other, by Clausius, "On the Kind of Motion which we call Heat."‡

* Phil. Mag. [4], xli. 393.

† Grundzüge einer Theorie der Gase; von A. Krönig. Pogg. Ann. xcix. 315.

‡ Ueber die Art der Bewegung welche wir Wärme nennen; von R. Clausius. Pogg. Ann. c. 353. See also a former paper by Clausius, "Ueber die bewegende Kraft der Wärme," ibid. lxxix. 394.

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules—each molecule being an aggregate of atoms—are supposed to be constantly moving forward in straight lines, and with a constant velocity, till they impinge against each other or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity, which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected. For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called, by Clausius, *the motion of the constituent atoms* (*Bewegungen der Bestandtheile*). The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the *temperature*. Now, the outward pressure exerted by the gas against the containing envelope, arises, according to our hypothesis, from the impact of a great number of gaseous molecules against the sides of the vessel. But, at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time, must vary inversely as the volume of the given quantity of gas; hence *the pressure varies inversely as the volume or directly as the density*, which is Mariotte's law.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into

the squares of their velocities; in other words, to the so-called *vis viva* or *living force* of the progressive motion. If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a two-fold force, and its number of impacts in a given time will also be doubled; hence the total pressure will be quadrupled.

Now we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by $\frac{1}{273}$ of its bulk for each degree centigrade. Hence the pressure or elastic force increases proportionately to the temperature reckoned from $-273°$ C.; that is to say, to the absolute temperature. Consequently, the *absolute temperature is proportional to the vis viva of the progressive motion.**

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and therefore the *vis viva* of the progressive motion must be an aliquot part of the entire *vis viva* of the gas; hence, also, the absolute temperature is proportional to the total *vis viva* arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its

* Suppose a vessel of the form of a rectangular parallelopiped, the length of whose sides are x, y, z, to contain n gas-molecules, each having the mass m. Suppose, also, the space enclosed by this vessel to be divided into $\frac{n}{6}$ equal cubes; and at a given instant let there be in each of these cubes six gas-molecules, moving severally in the directions $+x$, $-x$, $+y$, $-y$, $+z$, $-z$, and with the common velocity c. Let it also be supposed that the molecules exert no mutual action upon each other, but pass without hindrance from side to side of the vessel. It is required to determine the pressure which the gas exerts against one of the sides, yz, of the vessel. The pressure arising from the impact of a single gas-molecule is mca, if a denote the number of impacts which take place in a unit of time. Now, a molecule moving at right angles to yz, or parallel to x, strikes against yz every time that it passes over the space $2x$; therefore $a=\frac{c}{2x}$.

To find the total pressure P upon yz, the quantity, mca, must be multiplied

temperature by a given amount, is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume, is constant, a result which agrees with the experiments of Regnault, mentioned at page 429. This result may be otherwise expressed as follows: *The total vis viva of the gas is to the vis viva of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution; in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity.

The relations just considered between the pressure, volume and temperature of gases, presuppose, however, certain conditions of molecular constitution, which are, perhaps, never rigidly fulfilled; and accordingly, the experiments of Magnus and Regnault show (i. 13) that gases do exhibit slight deviations from Gay-Lussac and Mariotte's laws. What the conditions are which strict adherence to these laws would

by the number of molecules which move parallel to x, which number, since two atoms out of every six are parallel to x, is $\frac{n}{3}$. Hence $P = m \cdot c \cdot \frac{c}{2x} \cdot \frac{n}{3}$. And the pressure p upon a unit of surface of the side yz, is $p = m \cdot c \cdot \frac{c}{2x} \cdot \frac{n}{3} \frac{1}{yz}$; or if we put $xyz = v$, and leave out the constant factor:

$$p = \frac{nmc^2}{v}.$$

This expression shows that the pressure exerted upon a unit of surface is the same for each side of the vessel; also, that the pressure is inversely in proportion to the volume of the gas, which is Mariotte's law.

The product, mc^2, or the *vis viva* of an atom, is the expression of the temperature reckoned from the absolute zero, or —273° C.

If, in the preceding value of p, we put $mc^2 = t$, we have

$$p = \frac{nt}{v},$$

that is to say, when the volume is constant, the pressure varies directly as the absolute temperature (Krönig).

require, will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid* state, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately; the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear or rotatory. Moreover, when extraneous forces act upon the body, as in shocks, the molecules may permanently alter their relative positions.

In the *liquid state*, the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules and separate them completely from each other. A molecule is not permanently associated with its neighbours, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory and progressive movement of the molecules, but so regulated, that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous* state, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part, with a velocity equal to that with which they came together. The perfection

of the gaseous state, however, implies: 1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas. 2. That the time occupied in the impact of a molecule, either against another molecule or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts. 3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Mariotte's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced into the liquid state; but to a greater extent with vapours and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position with regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory, and vibratory movements, may be projected from the neighbouring molecules with such force as to throw it completely out of their sphere of action, before its projectile velocity can be annihilated by the attractive force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will, in consequence of the action just described, become more and more filled with these projected molecules, which will comport themselves within it exactly like a gas, impinging and exerting pressure upon the sides of the envelope. One of these sides, however, is formed by the surface of the liquid; and when a molecule impinges upon this surface, it

will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained, when the number of molecules projected in a given time into the space above, is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vaporisation. The density of the vapour required to ensure the compensation just mentioned, depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the rapidity of their movement within the liquid, that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapour must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There also it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapour-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards, equal to the external pressure tending to compress the vapour-bubble. The boiling point of the liquid will, therefore, be higher as the external pressure is greater.

According to this view of the process of vaporisation, it is possible that vapour may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapour

must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The *production* and *consumption of heat* which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the *work* done by the acting forces. This work is partly *external* to the body, partly *internal.* To consider first the *internal* work :

When the molecules of a body change their relative positions, the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the *vis viva* of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome,

and a corresponding loss of heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a movable obstacle, such as a piston, the molecules lose just so much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and, consequently, the temperature of the gas is raised.

When a liquid is converted into vapour, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being to a considerable extent affected by the external pressure. The liquefaction of a solid not being attended with much increase of volume, involves but little work; nevertheless, the atmospheric pressure does influence, in a slight amount, both the latent heat of fusion and the melting point.

LIGHT.

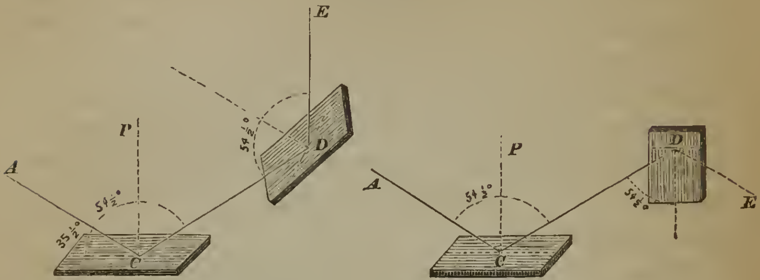
POLARISATION.

The phenomena of circular polarisation have lately acquired so much importance in chemistry, as to make it highly necessary for the student to be acquainted with them. But to render a description of these phenomena intelligible, a a few elementary explanations of the subject of polarisation in general must first be offered.

Suppose a ray of light, A C (fig. 24), to fall upon a plate

of glass (not silvered, but blackened at the lower surface) at C, making an angle of $54\frac{1}{2}°$ with the normal P C, or $35\frac{1}{2}°$

Fig. 24.



with the reflecting surface. This ray will be reflected in the direction C D, making an angle P C D = A C P, and in the same plane as A C and C P. Now suppose the reflected ray to fall upon a second surface of glass at the same angle of $54\frac{1}{2}°$ with the normal. If, then, the second mirror be so placed, that its plane of reflection is parallel to the plane of reflection from the first surface (see left-hand figure), then the ray will be reflected from the second surface in the direction D E, just as if it proceeded directly from a luminous source, and had not undergone previous reflection; but if the second mirror be so adjusted that its plane of reflection is perpendicular to that of the first (see right-hand figure), then the ray, C D, will not be reflected from it at all. In intermediate positions, still at the same angle of incidence, the ray, C D, will be partially reflected, the quantity of light in the reflected ray, D E, being greater as the planes of reflection of the two mirrors are more nearly parallel.

The ray, after reflection from glass at an angle of $54\frac{1}{2}°$ appears then to exhibit different properties, according to the direction in which it is a second time reflected; one side of the ray appearing to be reflectible, and the other side not so. The ray has now different properties on different sides, and is said to be *polarised.*

The angle, $54\frac{1}{2}°$, is called the polarising angle for glass.

For every medium there is a particular polarising angle, the magnitude of which depends upon the refracting power of the medium.* Now, as the different coloured rays which compose white light, differ in refrangibility (i. 104), there must be for each coloured ray a distinct polarising angle. Hence it is evident that only homogeneous light can be completely polarised by reflection. Solar light, or ordinary gas or candle-light, can never be made to disappear completely in the manner above mentioned.

The plane in which a polarised ray is most easily reflected is called its *plane of polarisation:* it coincides with the plane of reflection (or of incidence).

Light is also polarised by refraction, and the refracted ray is polarised in a plane perpendicular to the plane of refraction, or of incidence, and, therefore, also perpendicular to the plane of polarisation of the reflected ray; so that it would be reflected from a surface of glass at an angle of $54\frac{1}{2}°$, just under the circumstances in which the ray polarised by reflection would not. Light, however, is never completely polarised by one refraction; but by successive refractions through a number of surfaces of glass, or other medium, it may be brought within any assigned limit of complete polarisation.

* In all cases, the polarising angle, A C P (fig. 25), is that for which the refracted ray, C D, is perpendicular to the reflected ray, C B. Let m denote the index of refraction, then:

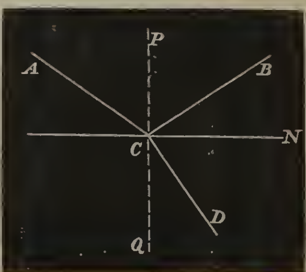
$$m = \frac{\sin \mathrm{ACP}}{\sin \mathrm{QCD}};$$

but angle A C P = B C P [$= \theta$]; and since B C is perpendicular to C D, and Q C to C N, angle Q C D = B C N = $90° - \theta$; therefore

$$m = \frac{\sin \theta}{\cos \theta} = \tan \theta;$$

that is to say, *the polarising angle is the angle whose tangent is equal to the index of refraction.*

Fig. 25.



All crystalline bodies not belonging to the regular system, possess the power of *double refraction* (i. 103), that is to say, a ray of light entering such a medium is split up into two rays of equal intensity, which traverse the crystal in different directions. In all such media, however, there are either one or two directions in which double refraction does not take place, and these lines are called the *optic axes* of the crystal. Transparent calcspar, or Iceland spar, which crystallises in rhombohedrons, and exhibits double refraction more distinctly than any other substance, is a crystal with one optic axis, the direction of that axis being parallel to the line joining the obtuse summits of the rhomb. A ray traversing the crystal in a direction parallel to this axis is not divided into two; but in all other directions the ray is doubly refracted; and the two rays into which it is thus divided are both completely polarised, the one in the *principal section*, that is to say, in a plane passing through the optic axis and the direction in which the ray traverses the crystal; the other at right angles to that plane. The ray which is polarised in the principal section follows the ordinary laws of refraction, remaining always in the plane of incidence, and having for all incidences a constant index of refraction; but the ray polarised perpendicularly to the principal section follows different laws of refraction, its direction not being confined within the plane of incidence, unless that plane coincides with or is perpendicular to the principal section, and its index of refraction, excepting in the last-mentioned case, varying continually with the angle of incidence. The former of these rays is called the *ordinary*, the latter the *extraordinary* ray.

When these two oppositely polarised rays fall on a plate of glass at the angle of 54½°, so placed that the plane of reflection is parallel to the principal section of the crystal, the ordinary ray is reflected, and the extraordinary ray is not, the contrary effect taking place when these planes are at

right angles to each other. When the plane of reflection is inclined to the principal section at any angle between 0° and 90°, both rays are reflected, but with different intensities.

Nichol's Prism.—It is often desirable to get rid of one of the images produced by a double-refracting crystal. This is effected by the arrangement shown in fig. 26, which consists of two similar prisms of calcspar, A B C D, C D E F, cemented together with Canada balsam at the faces, C D. The faces, A B, E F, are cut so as to make an angle of 68° with the obtuse edges, A E, B F, of the natural crystal (the natural faces make an angle of 71° with the obtuse edges), and the faces, C D, are perpendicular to A B and E F. With this arrangement, it is found that of the two rays, *n o*, *n e*, into which an incident ray, *m n*, is divided, the ordinary ray, *n o*, on reaching the surface of Canada balsam (whose index of refraction is less than that of the ordinary and greater than that of the extraordinary ray), suffers total reflection in the direction *o* P, while the extraordinary ray passes on in the direction *e f*, and emerges in *f g*, parallel to *m n*. An eye placed at *f*, therefore, sees but one image, viz., that formed by the extraordinary ray. This apparatus, called a Nichol's prism, is of great use in experiments with polarised light. For, as it transmits only the extraordinary ray, a beam of ordinary light passing through it will be polarised in a plane perpendicular to the principal section—that is to say, to the shorter diagonal of the rhomb, *a b* (fig. 27); and a ray, already polarised, will be stopped by the prism if its plane of polarisation is parallel to *a b*, but will pass freely

Fig. 26.

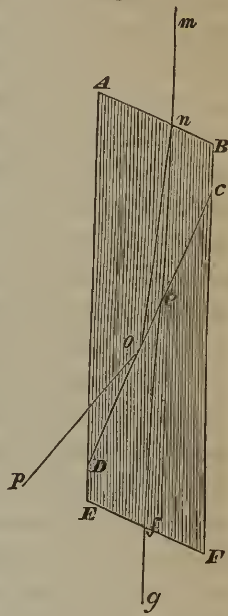
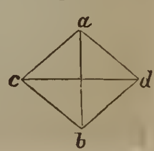


Fig. 27.



through it when the plane of polarisation is perpendicular to *a b*, or parallel to the longer diagonal, *c d*. Hence, also, two Nichol's prisms, placed one behind the other, appear perfectly opaque when their principal sections are at right angles to each other, perfectly transparent when the principal sections are parallel, and transmit light with diminished intensity in intermediate positions.

Polarisation by Tourmalines. — The tourmaline, which is a crystallised mineral having one optic axis, possesses the remarkable property of transmitting light only when polarised in a plane perpendicular to that axis. Hence, a plate of tourmaline cut with faces parallel to the optic axis, acts exactly like a Nichol's prism, and may be used in the same manner. It is, however, less convenient, on account of its colour, which, in the best tourmalines, is rather a dark yellow-brown.

Nature of Polarised Light.—Light is supposed to consist of undulations excited in an ethereal medium pervading all space, and filling up the intervals between the particles of ponderable bodies. Moreover, the particles of this ether are supposed to vibrate, not in the direction of the ray, like the particles of air in conveying sound, but in planes at right angles to the length of the ray, like the transverse vibrations of a stretched cord.

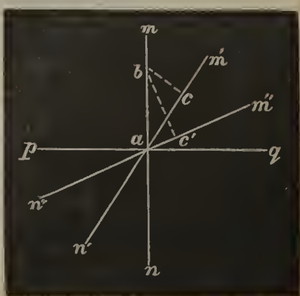
Further, the difference between ordinary and polarised light, is supposed to be this: that in the former, the particles of the ether vibrate in all imaginable directions, at right angles, to the length of the ray; while, in the latter, they are confined to one particular plane. Thus, if A (fig. 28) represents the projection of an unpolarised ray, travelling at right angles to the plane of the paper, the particles of the ether at

Fig. 28.

all points of this ray vibrate parallel to the plane of the paper, but some may move in the direction *a a′*, others in *b b′*, *c c′*, *d d′*, &c. Now imagine all these vibrations to be reduced to one plane, in the direction *a a′*, for example. Then the ray will become polarised. In fact, since its particles now vibrate in one direction only, it is no longer a matter of indifference whether the ray is presented to a reflecting surface on one side or the other; whereas the unpolarised ray, whose particles vibrate in all directions, will be reflected in the same manner on whichever side it meets the surface of any medium.

Now, from considerations into which we cannot at present enter, it is found that a plate of tourmaline transmits only those vibrations which are parallel to its axis. Since then, a ray of polarised light is transmitted through a tourmaline only when its plane of polarisation is perpendicular to the axis of the tourmaline (p. 461), it follows that *the plane of polarisation of the ray is perpendicular to the plane of vibration.* Hence, also, the plane of vibration of a ray polarised by reflection is at right angles to the plane of incidence (or of reflection); the plane of vibration of a ray polarised by refraction is parallel to the plane of incidence; and of the two rays into which a beam of light is divided by double refraction through a rhomb of calcspar, the ordinary ray vibrates at right angles to the principal section, and the extraordinary ray parallel to that section. The vibrations of a ray polarised by passing through a Nichol's prism, are, therefore, parallel to to the principal section, that is, to the shorter diagonal of the prism (fig. 27).

Fig. 29.



Let *m n* (fig. 29), be the plane of vibration of a polarised ray moving at right angles to the plane of the paper, and meeting it at the point *a*. If this ray enters

a plate of tourmaline, whose axis is parallel to $m\,n$, or a Nichol's prism, whose principal section is in that direction, the ray will be transmitted with its full intensity. But if the axis of the tourmaline or the principal section of the prism be turned round into the position $m'\,n'$, the intensity of the transmitted light will be diminished, because the tourmaline or the prism will only transmit vibrations in the direction $a\,m$, and there is always a loss of power in changing the direction of motion. Let $a\,b$ represent the utmost length of the excursion of a particle of the ether in the original direction of vibration, in other words, the original intensity of the light. Draw $b\,c$ at right angles to $a\,m'$; then $a\,c$ represents the component of the force $a\,b$ in the direction $a\,m'$, and $a\,c$ is clearly less than $a\,b$. If the tourmaline or the prism be turned still further into the position $m''\,n''$ the reduced portion of the intensity $a\,c'$ will be found to be still less; and, lastly, when the axis or the principal section is perpendicular to $m\,n$, the reduced portion of the motion becomes equal to nothing, and there is no light transmitted. Generally, if u be the original intensity of the light, and θ the angle between the old and new planes of vibration, the reduced intensity will be $u \cos \theta$.

Circular Polarisation.—Some media possess the singular property of changing the direction of vibration of a ray of polarised light; in other words, of causing the plane of polarisation to rotate through a certain angle, either to the right or to the left. This property is exhibited in a remarkable degree, by quartz or rock-crystal, a mineral which crystallises in six-sided prisms terminated by six-sided pyramids, the axis being a straight line joining the two pyramidal summits. Suppose now, a ray polarised by passing through a Nichol's prism to be viewed through another such prism, having its principal section at right angles to that of the first. The field will, of course, appear dark. Then let a plate of quartz, bounded by parallel faces cut perpendicularly to its axis, be interposed between the two prisms.

Immediately the field of view will appear brilliantly illuminated and coloured, exhibiting a tint of red, yellow, green, blue, &c., according to the thickness of the quartz-plate. If the Nichol's prism, which serves as the eye-piece, be turned on its axis, the colours will go through the regular prismatic series, from red to violet, or the contrary, according to the direction of rotation; but no alteration of colour is produced by rotating the quartz-plate while the eye-piece remains stationary. Exactly similar effects are produced if either of the Nichol's prisms be replaced by a tourmaline or a glass reflector, or a bundle of glass plates which polarise by ordinary refraction; but the two Nichol's prisms form by far the most convenient apparatus, and we shall therefore suppose them to be always used. For distinction, the one is called the polarising prism or polariser, the other, the eye-piece.

To understand the phenomena just described, we must examine what takes place when homogeneous light is used. Suppose, then, a plate of dark-red glass coloured with red oxide of copper, to be interposed anywhere between the two prisms placed as before, with their principal sections at right angles, so that no light is transmitted by the eye-piece. On interposing the plate of quartz, a red light immediately makes its appearance, and, to render the field again dark, it is necessary to turn the eye-piece through a certain angle, either to the right or to the left. Now, as the Nichol's prism stops a ray of light only when the plane of vibration of that ray is perpendicular to its principal section, it follows that the ray which has traversed the quartz must have had its plane of vibration thereby deflected through an angle equal to that through which the eye-piece has been moved. This effect is called *circular polarisation.*

Precisely similar effects are produced with yellow, green, violet, or any other kind of homogeneous light; but the angle of rotation varies according to the nature of the ray, being least for red, and greatest for violet light.

Some crystals of quartz rotate the plane of polarisation of a ray to the right, others to the left; the former are called *right-handed*, the latter *left-handed quartz*. But in whichever direction the rotation takes place, a plate of quartz of given thickness always produces the same amount of angular deviation for a ray of given refrangibility; and for plates of different thickness, the deviation for any particular ray increases in direct proportion to the thickness. The following table gives the angles of deviation for the principal rays of the spectrum produced by plates of quartz of the thickness of 1 millimeter and 3·75 millimeters.

Colours.	Angle of Rotation.	
	Plate 1 mm. thick.	Plate 3·75 mm. thick.
Medium red	15°	56¼°
„ orange . . .	19	71¼
„ yellow . . .	24	90
„ green . . .	27	101¼
„ blue	32	120
„ indigo . . .	38	142½
„ violet	44	165

We can now explain the succession of colours produced when ordinary daylight is used. Suppose a beam of white light, polarised by a Nichol's prism, whose principal section is parallel to A A′ (fig. 30), to pass through a plate of right-handed quartz, 3·75 mm. thick. The vibrations of the several coloured rays composing the beam of polarised light, are all at first parallel to A A′; but by passing through the quartz, their planes of vibration are deflected through the several angles given in the above table,

Fig. 30.

the red ray then vibrating in the line $r r'$, the yellow in $y y'$, the violet in $v v'$, &c. Now, let the ray be viewed through another Nichol's prism, placed with its principal section also parallel to A A′; then, by reference to the explanation given at page 463, it will be seen that the red and violet rays will be transmitted with but slightly diminished intensity, the orange and blue with less, the yellow with still less, and the green not at all. The result will, therefore, be a purple tint. Now let the eye-piece be turned from left to right. As the principal section passes successively over the lines $r r'$, $o o'$, &c., the red, orange, yellow, &c., will, in succession, be more fully transmitted than the other rays, so that a succession of tints will be produced agreeing nearly with the colours of the spectrum and following in the same order, from red through yellow to violet. If the eye-piece be turned the contrary way, the order of the tints will be reversed. If the quartz were left-handed, the phenomena would be precisely similar, excepting that the colours would change from red through yellow to violet, when the eye-piece was turned from right to left.

Similar changes of colour will be produced with a plate of quartz of any other thickness; but the tint produced at any given inclination of the polariser and eye-piece, will of course be different.

The tint produced with a quartz-plate 3·75 mm. thick, when the prncipal sections of the polariser and eye-piece are parallel to one another, deserves particular notice. This tint, as already observed, is a purple, and moreover changes very quickly to red or to violet, when the eye-piece is turned one way or the other, the change of colour thus produced being, in fact, very much more rapid and decided than in any other part of the circuit. It is accordingly distinguished by the term *sensitive tint*, or *transition-tint* (*couleur sensible, teinte de passage*). On account of the facility and certainty with which it may be recognised, it is frequently

adopted as the standard tint in measuring the angles of rotation produced by different substances; it is, in fact, much easier to determine when this particular colour makes its appearance, than to seize the exact moment when a ray of red, yellow, or other homogeneous light completely disappears.

The rotatory power of quartz is essentially related to its crystalline form. It is not exhibited by opal, or any other amorphous variety of silica, or by silica dissolved in potash or fused by the oxy-hydrogen blowpipe. The same is true with regard to a few other inorganic compounds possessing the rotatory power, viz. chlorate of soda, bromate of soda, and acetate of uranic oxide and soda; these salts exhibiting that power only when crystallised, not in solution.

Circular Polarisation in Organic Bodies.—The power of rotating the plane of vibration of a polarised ray, is much more widely diffused in the organic, than in the inorganic world; moreover, inorganic bodies possess it in the liquid, as well as in the crystalline state. Among organic compounds which rotate the plane of polarisation to the right, may be mentioned:—Cane-sugar, grape-sugar, diabetic sugar, milk-sugar, dextrin, camphor, asparagin, cinchonine, quinidine, narcotine, tartaric acid, camphoric acid, aspartic acid, oil of lemons, castor-oil, croton-oil. The following rotate to the left:—uncrystallisable sugar of fruits, starch, albumen, amygdalin, quinine, nicotine, strychnine, brucine, morphine, codeine, malic acid, anti-tartaric acid, oil of turpentine, oil of valerian.

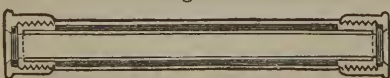
By passing a polarised ray through tubes of different lengths, filled with the same solution of cane-sugar, or other rotatory substance, it is found that the angle of deviation is proportional to the length of the column of liquid; and, by filling the same tube with solutions containing different quantities of sugar, &c., it is found that the angle of deviation is proportional to the quantity of the substance contained in a column of given length. Generally, then, the angle of deviation is proportionate to the number of active particles which the light has to pass.

If, then, ε be the quantity of active substance contained in a unit of weight of the solution, l the length of the column, and α the observed angle of rotation for a particular tint, the transition-tint, for example, the angle of rotation for the unit of length, and supposing the entire column to be filled with the optically active substance, will be $\frac{\alpha}{\varepsilon\, l}$. But as the solution of a substance is often attended with condensation of volume, it is best, in order to obtain a measure of the rotatory power, independent of such irregularities, to refer the observed angle of deviation to a hypothetical unit of density, that is to say, to divide the quantity $\frac{\alpha}{\varepsilon\, l}$ by the density δ of the solution. The fraction thus obtained, viz., $[\alpha] = \frac{\alpha}{\varepsilon\, l\, \delta}$, is called the *specific rotatory power*, and expresses the angle of rotation which the pure substance in a column of the unit of length and density $= 1$ would impart to the ray corresponding to the transition-tint. For example, a solution containing 155 milligrammes of cane-sugar in a gramme of liquid, has a specific gravity $= 1{\cdot}06$, and deflects the transition-tint by 24°, in a column 20 centimeters long; its specific rotatory power is therefore —

$$[\alpha] = \frac{24}{0{\cdot}155\ .\ 20\ .\ 1{\cdot}06} = 7{\cdot}3^\circ$$

Saccharimetry. — An important practical application of the principles just explained relates to the determination of the quantity of sugar contained in saccharine solutions. The apparatus used for this purpose consists of a glass tube (fig. 31), surrounded with a case of wood or brass, and closed

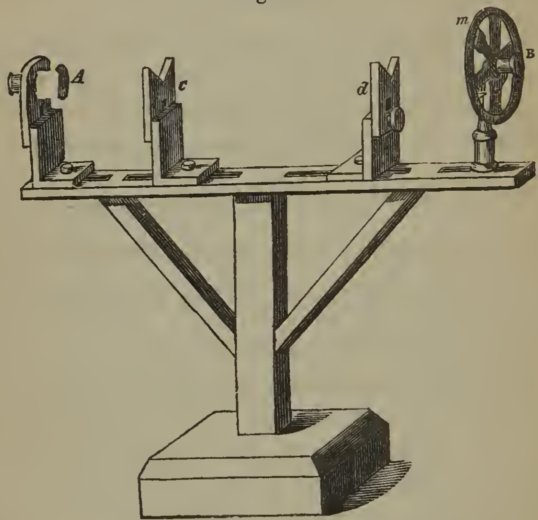
Fig. 31.



at both ends with plate-glass discs ground to fit water-tight

and pressed against the tube by means of screw-caps. The tube being completely filled with the liquid, is placed on the supports, *c d* (fig. 32), between two Nichol's prisms, one of which, A, serves as a polariser, the other, B, as an eye-piece. The latter carries a vernier, *m*, moving round a

Fig. 32.



graduated circle. The simplest way of using this apparatus is to interpose between the tube and the polariser a glass coloured with sub-oxide of copper, the tint of which corresponds with the red of the fixed line C of the spectrum—and having set the eye-piece with its principal section at right angles to that of the polariser (which makes the field of view dark so long as the tube is not interposed), to adjust the tube in its place, and turn the eye-piece round till the red light completely disappears. The angle through which the eye-piece is turned measures the deviation produced by the saccharine liquid.

A solution of 164·71 grammes of pure and dry cane-sugar in a litre of water, produces in a tube, 20 centimeters long,

an optical effect equal to that of a plate of right-handed quartz, 1 millimeter thick, that is to say, it turns the plane of polarisation of the red ray corresponding to the fixed line C, through an angle of 15·3°. Hence, if any other solution of cane-sugar in a tube of the same length produces a deviation of a degrees, one litre of that solution will contain

$$\frac{a}{15{\cdot}3} \,.\, 164{\cdot}71 \text{ grammes of sugar.}$$

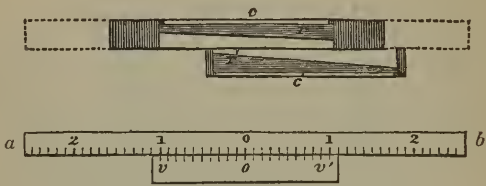
The direct measurement of the rotation of the red ray is, however, by no means the best mode of observation, because, as already observed (p. 468), it is difficult to tell with precision when the light completely disappears. For this reason it is better to introduce behind the polarising prism, instead of the red glass, a plate of quartz 3·75 millimeters thick, which, when the polariser and eye-piece are set with their principal sections parallel, exhibits the *transition-tint.* The interposition of the saccharine liquid, which rotates to the right, causes this tint to change; and the rotation is measured by the number of degrees through which the prism must be turned to restore the transition-tint.

Greater exactness is obtained by using a double plate of quartz 3·75 millimeters thick, one-half being composed of right-handed, the other half of left-handed quartz. Such a plate will exhibit the transition-tint with perfect uniformity on both halves, when the polariser and eye-piece are set with their principal sections parallel; but on turning the eye-piece to the right, one-half of the plate will incline to red, and the other to blue. The same change will, of course, take place on introducing the tube containing the saccharine liquid; and to restore the uniformity of tint, the eye-piece must be turned a certain number of degrees the contrary way. If the liquid has but a slight rotatory power, this method is quite satisfactory; but if the rotatory power is considerable, an

error arises from the different angles of rotation imparted to the different coloured rays.

To obviate this last source of inaccuracy, a contrivance, called the *compensator*, has been invented. It consists of two prismatic plates of quartz, *r r′* (fig. 33), having their faces,

Fig. 33.



c c′, perpendicular to the crystallographic axis, and the opposite faces inclined to this axis at equal angles. These prisms are introduced into the polarising apparatus between the tube and the eye-piece, and one of them is made to slide over the other by means of a rack and pinion, so that the two together form a plate of variable thickness. To the frame of one of these prisms is attached a linear scale, *a b*, and to the other an index, or a vernier, *v v′*. One hundred divisions of the scale correspond to an increase of 1 millimeter in the thickness of the compound plate. Suppose now these two prisms to consist of left-handed quartz; a flat plate of right-handed quartz, whose thickness is equal to that of the two compensating prisms together when the index points to 0°, is likewise introduced between the tube and the eye-piece. This plate then completely neutralises the action of the compensator, and the effect is the same as if neither the compensator nor the plate of right-handed quartz were introduced, the double quartz-plate (p. 471) still exhibiting the transition-tint on its two halves, when the tube containing the saccharine solution is not in its place. Now let the tube containing the dextro-rotatory saccharine liquid be introduced. Immediately the two halves of the double-plate assume different

colours; and to restore the uniformity of tint, the compensator must be shifted so as to give the combined left-handed prisms a greater thickness. Suppose that, to produce this compensation, the index is moved through eighteen divisions of the scale. Then the rotatory action of the liquid in the tube is equal to that of a quartz-plate having a thickness of $\frac{18}{100}$ of a millimeter, that is to say, it turns the red ray through an angle of $15{\cdot}3° \times \frac{18}{100} = 2\frac{3}{4}°$.

In order that the preceding method may be directly applied to determine the strength of a solution of any optically active substance, it is necessary: 1. That the solution contain only *one* such substance. 2. That the quantity of the active substance present be proportioned to the angle of rotation. 3. That the rotation of the red ray be known for one given degree of concentration.

Now, in determining the quantity of crystallisable sugar in the syrups obtained from plants, in molasses, &c., a difficulty arises from the presence of other kinds of sugar, viz., glucose, and, more especially, the uncrystallisable sugar of fruits, which rotates to the left. This difficulty may, in most cases, be obviated by boiling the liquid with hydrochloric acid, whereby the crystallisable sugar (cane-sugar) is converted into the lævo-rotatory sugar of fruits, while the other kinds of sugar remain unaltered. The rotatory power of cane-sugar is not sensibly affected by heat; but that of uncrystallisable sugar decreases considerably as the temperature rises. Thus, when cane-sugar is heated with hydrochloric acid to 68° C., the resulting fruit-sugar exhibits at different temperatures the following rotatory powers:—

Temperature	10°	15°	20°	25°	30°	35°
Rotatory power (that of cane-sugar) = 100°	39	36	34	3·15	29	26·5

Suppose, now, a solution of cane-sugar containing 164·71 grammes in a litre, which, in a column 20 centimeters long,

deflects the red ray 15·3° to the right, to be heated to 68° C., with $\frac{1}{10}$ of its volume of hydrochloric acid, and the liquid, after cooling to 15° C., to be introduced into the polarising apparatus in a tube 22 centimeters long, which will contain the same number of atoms of sugar as a tube 20 centimeters long of the liquid before the addition of the acid. The red ray will then be deflected to the left by $0{\cdot}36 \times 15{\cdot}3° = 5{\cdot}5°$. Consequently, the difference in the positions of the eye-piece before and after the conversion will amount to $15{\cdot}3° + 5{\cdot}5° = 20{\cdot}8°$.

If, then, any mixed solution of cane-sugar and uncrystallisable fruit-sugar, containing 164·71 grammes of sugar in a litre, be treated as above, and the difference in the positions in the eye-piece before and after the conversion be 5·2°, the temperature being 15° C., the amount of crystallisable sugar in the mixture is $\frac{5{\cdot}2}{20{\cdot}8} . 164{\cdot}71 = 41{\cdot}2$ grammes.*

If the mixture contains grape or starch-sugar mixed with cane-sugar, it must be heated to 80° C. before being introduced into the saccharimeter, because the rotatory power of grape or starch-sugar decreases considerably after a while

* Let n be the observed deviation before inversion, n' the dextro-rotation produced by the crystallisable sugar, n'' the lævo-rotation produced by the uncrystallisable fruit-sugar. Also, let n_1 be the observed deviation in a column of liquid of the same length, after the liquid has been heated with $\frac{1}{10}$ of its volume of hydrochloric acid; and suppose that a quantity of cane-sugar which produces a deviation of n' to the right, yields, when thus treated, a quantity of uncrystallisable sugar, which produces a deviation of Kn' to the left (at 15° C., $K = 0{\cdot}36$). Then, for the determination of n' and n'', we have the two equations:—

$$n = n' - n''$$
$$\tfrac{10}{9} n_1 = n'' + Kn'$$

A mixture of cane-sugar with starch-sugar or grape-sugar may be treated in exactly the same manner, since only the cane-sugar has its direction of rotation reversed; and in this case, n' and n'' will be determined by the equations:—

$$n = n' + n''$$
$$\tfrac{10}{9} n_1 = n'' - Kn'$$

at ordinary temperatures, but quickly attains its minimum value when the liquid is heated to 80°.

If grape or starch sugar is present together with uncrystallisable fruit-sugar, the problem is indeterminate, because neither of these sugars has its rotating action reversed by treatment with acids.

The following table contains a few of the results obtained by the method just described. If the liquid to be examined contains nothing but crystallisable sugar, we have merely to look in the last column but one for the number of degrees read off on the compensator; and the corresponding number in the last column gives the number of grammes of sugar in a litre of the liquid. If other optically active substances are present, and inversion is consequently necessary, the results are found by means of the readings in the first six columns.

Table for the Analysis of Saccharine Solutions.*

Sum or difference of the readings before and after the inversion of the sugar, the last reading being made at the temperature of						Degrees.	Grammes of sugar in a litre.
10°	15°	20°	25°	30°	35°		
1·4	1·4	1·3	1·3	1·3	1·3	1	1·64
13·9	13·6	13·4	13·1	12·9	12·6	10	16·47
27·8	27·3	26·8	26·3	25·8	25·3	20	32·94
41·7	40·9	40·2	39·4	38·7	37·9	30	49·41
55·6	54·6	53·6	52·6	51·6	50·6	40	65·88
69·5	68·2	67·0	65·7	64·5	63·2	50	82·35
83·4	81·9	80·4	78·9	77·4	75·9	60	98·82
97·3	95·5	93·8	92·0	90·3	88·5	70	115·29
111·2	109·2	107·2	105·2	103·2	101·2	80	131·76
125·1	122·8	120·6	118·3	116·1	113·9	90	148·23
139·0	136·5	134·0	131·5	129·0	126·5	100	164·71
152·9	150·1	147·4	144·6	141·9	139·1	110	181·18
166·8	163·8	160·8	157·8	154·8	151·8	120	197·65
180·7	177·4	174·2	170·9	167·7	164·4	130	214·21

* This table is extracted from the much more extensive one given in the "Traité de Chimie Générale" par Pelouze et Fremy. Paris, 1855, t. iv. pp. 620—622.

Relations between Rotatory Power and Crystalline Form.—It has already been observed that silica and a few other inorganic bodies exhibit circular polarisation, only when crystallised. Moreover, crystals of the same substance—quartz, for example—which exert opposite actions on polarised light, often exhibit a remarkable opposition in their crystalline forms. Thus, the ordinary form of quartz, the six-sided prism with pyramidal six-sided summits, is sometimes found modified in the manner shown in figs. 34, 35, the solid angles formed by the meeting of two pyramidal with two

Fig. 34.

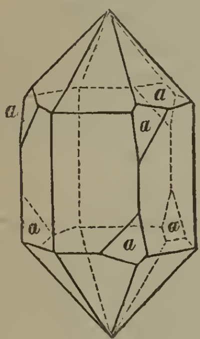
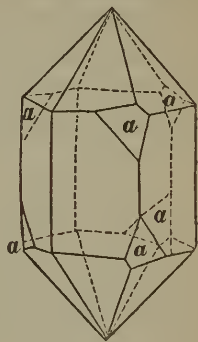


Fig. 35.



prismatic faces, being truncated with faces, *a*, obliquely inclined to the faces of the prism; these truncation faces, however, are only six in number, whereas to form a complete holohedral combination (since these faces are unequally inclined to those of the prism), there should be twenty-four of them, two at each of the twelve angles above-mentioned: the form is therefore tetartohedral.* But, further, these

* *Holohedral* forms are those which are bounded by similar faces occurring in the greatest possible number consistent with the law of symmetry which determines their position; if the number of such faces is only one-half of what it might be, the form is *hemihedral;* if only one-fourth, it is *tetartohedral.* The regular octohedron is a holohedral crystal, and the tetrahedron is the hemihedral form corresponding to it; similarly, the rhombohedron is the hemihedral form of the double six-sided pyramid. Hemihedral and tetartohedral forms often occur associated with holohedral forms in the same crystal.

tetartohedral faces are not always placed alike, occurring in some crystals on the right of a prismatic face above, and on the left below, and the contrary in others, as shown in the above figures. The two forms of crystal thus produced, though their faces are alike in number and in form, are evidently not superposible, but the one may be regarded as the reflected image of the other. Now, the crystals of the one kind invariably exhibit dextro-rotatory, and those of the other kind lævo-rotatory, power. The same kind of opposite tetartohedry, and accompanied by a corresponding opposition of rotatory power, is found in the few other inorganic compounds (p. 468) which exhibit circular polarisation.

This remarkable relation between rotatory power and crystalline form is, however, much more strikingly exhibited by certain organic compounds.

Tartaric acid and its salts turn the plane of polarisation to the right; racemic acid, which is identical in chemical composition with tartaric acid, and agrees with it in nearly all its chemical relations, has no action whatever on polarised light, either in the free state of the acid or when combined with bases. Now, the crystals of tartaric acid and the tartrates are *hemihedral*, those of racemic acid and the racemates, with one exception, are *holohedral.* The exception alluded to is the racemate of soda and ammonia. A solution of racemate of soda and racemate of ammonia, in equivalent proportions, yields by evaporation crystals of a double salt, the form of which is represented in figs. 36, 37.

It is a right rectangular prism P, M, T, having its lateral edges replaced by the faces b', and the intersection of these latter faces, with the face T, replaced by a face h. If the crystal were holohedral, there would be eight of these faces, four above, and four below; but, as the figures show, there are but four of them, placed alternately: moreover, these hemihedral faces occupy in different crystals, not similar, but opposite positions; so that, as in the case of quartz, the

one kind of crystal is, as it were, the reflected image of the other.

Fig. 36.

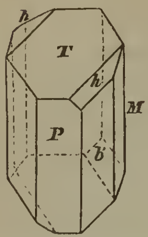
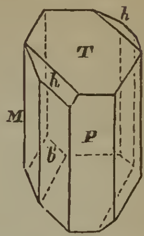


Fig. 37.



But further; by carefully picking out the two kinds of crystals, and dissolving them separately in water, solutions are obtained, which, at the same degree of concentration, exert equal and opposite actions upon polarised light, the one deflecting the plane of polarisation to the right, the other, by an equal amount, to the left. Moreover, the solutions of the right and left-handed crystals, yield, by evaporation, crystals, each of its own kind only; and by mixing the solutions of these crystals with chloride of calcium, lime-salts are obtained, which, when decomposed by sulphuric acid, yield acids, agreeing with each other in composition, and in every other respect, except that their crystalline forms exhibit opposite hemihedral modifications, and their solutions, when reduced to the same degree of concentration, exhibit equal and opposite effects on polarised light.

Of the two acids thus obtained, the one which turns the plane of polarisation to the right is identical in every respect with ordinary tartaric acid. The other may be called, for distinction, *antitartaric acid.* When equal weights of these two acids are dissolved in water, and the solutions mixed, a liquid is obtained, which has no action whatever on polarised light, and yields by evaporation, holohedral crystals of *racemic acid.* A similar result is obtained by mixing equal quantities of any of the salts of the two acids, excepting the double salt of soda and ammonia.

Hence it appears that racemic acid, a body which has no action upon polarised light, and crystallises in holohedral forms, is a compound of two acids (tartaric and antitartaric*), which have equal and opposite effects on polarised light, and crystallise in similar but opposite hemihedral forms. There is also another property in which these acids differ, viz. in their pyro-electric relations. The crystals of both these acids become electric when heated, but the corresponding extremities of the two exhibit opposite electrical states. Racemic acid is not pyro-electric.

Tartaric acid may be converted into racemic acid by the action of heat, provided only it be associated with some substance which will enable it to bear a somewhat high temperature without decomposing. There are many substances whose effect on polarised light is altered by heat. This is remarkably the case with the alkaloids of the cinchona bark. When cinchonine, or any of its salts (which rotate to the right), is heated in such a manner as not to produce decomposition, it is transformed into an isomeric alkaloid, *cinchonicine*, which turns the plane of polarisation to the left. Similarly, quinine, which rotates the plane of polarisation to the left, is converted by heat into quinicine, which turns it to the right. Now, when tartrate of cinchonine is heated, it is first converted into tartrate of cinchonicine, and if the heat be then continued, the change extends to the tartaric acid, half of which is converted into antitartaric acid. If the process be stopped at a certain point, and the fused mass treated with water, a solution is obtained which yields, first, crystals of antitartrate, and afterwards, of tartrate of cinchonicine. But if the heat be longer continued, the two acids unite, and form racemate of cinchonicine, from which racemic acid may be prepared, identical in every respect with ordinary racemic acid, and separable by the same means into the two opposite tartaric acids.

* Thence also called respectively *dextro-racemic* and *lævo-racemic* acids.

But, what is very remarkable, there is formed at the same time a modification of tartaric acid, which has no action whatever on polarised light, and yet is not separable into the two opposite acids. In fact, when the fused mass obtained by heating tartrate of cinchonine is treated with water, and chloride of calcium added, a precipitate is formed, consisting of racemate of lime, and the filtrate, if left at rest, deposits crystals of the lime-salt of *inactive tartaric acid.*

There are other organic compounds which are also optically active in their ordinary forms, but exhibit inactive and inseparable modifications. Malic acid, as it exists in fruits, turns the plane of polarisation to the right; so likewise does aspartic acid obtained by the action of acids and alkalies on asparagin. Now both these acids may be formed from fumaric acid, an optically inactive substance. Acid fumarate of ammonia is $C_8H_3(NH_4)O_8 = C_8H_7NO_8$, which is also the formula of aspartic acid, and this acid is actually formed by heating the acid fumarate of ammonia. But the aspartic acid thus produced is, like fumaric acid, optically inactive. Again, aspartic acid is converted into malic acid by the action of nitrous acid:—

$$\underbrace{C_8H_7NO_8}_{\text{Aspartic acid.}} + NO_3 = \underbrace{C_8H_6O_{10}}_{\text{Malic acid.}} + 2N + HO.$$

Both active and inactive aspartic acids undergo this transformation; but active aspartic acid yields active malic acid, and inactive aspartic acid yields inactive malic acid. Neither inactive aspartic nor inactive malic acid can be separated into two acids oppositely active.

Common oil of turpentine possesses considerable dextrorotatory power; but the isomeric substance obtained by heating the artificial solid camphor of turpentine with quicklime is optically inactive.

Fusel oil has lately been shown by Pasteur to be a mixture of two kinds of amylic alcohol, which differ slightly in

boiling point. One of these alcohols is optically active, the other inactive.

Rotatory Power induced by Magnetic Action.—Faraday has made the remarkable discovery, that bodies which, in their ordinary state, exert no particular action on polarised light, acquire the circular-polarising structure when subjected to the action of powerful electric or magnetic forces. A polarised ray passing along the axis of a prism or cylinder of any transparent substance, such as water or glass, has its plane of polarisation deflected to the right or left, as soon as the medium is subjected to the action of an electric current passing round it at right angles to the axis, or to that of two powerful opposite magnetic poles, so placed that their line of junction shall be parallel to the axis of the column of the transparent substance. The rotation ceases as soon as the electric or magnetic force ceases to act; its amount varies directly as the strength of the current; and its direction changes with that of the current or of the magnetic force. If the medium has a rotatory power of its own, the total effect is equal to the sum or difference of the natural and induced rotations, according as the electric or magnetic force acts with or against the natural rotatory power of the medium.

CHANGE OF REFRANGIBILITY OF LIGHT.—FLUORESCENCE.

It was observed some years ago by Sir John Herschel, that a solution of sulphate of quinine, though perfectly colourless by transmitted light, exhibits in certain aspects a peculiar blue colour. This blue light was found to be produced only by a very thin stratum of the liquid adjacent to the surface by which the light entered; and the incident beam, after having passed through the stratum from which the blue light came, was not sensibly weakened or coloured, but had lost the power of producing the usual blue colour when admitted into another

solution of sulphate of quinine. Light thus modified was said by Sir J. Herschel to be *epipolised.*

Similar phenomena were observed by Sir D. Brewster in an alcoholic solution of chlorophyll, the green colouring matter of leaves, the path of a beam of sunlight admitted into the green solution being marked by a bright light of a blood-red colour. The same appearance was afterwards observed in various vegetable solutions and essential oils, and in some solids. Brewster distinguished this phenomenon by the name of *internal dispersion,* attributing it to the irregular reflection of the light from coloured particles suspended in the liquid, and was of opinion that Herschel's epipolic dispersion was only a particular case of this internal dispersion.

The true explanation of these remarkable phenomena has, however, been given by Professor Stokes *, who has submitted the whole subject to the most searching investigation, and shown that the peculiar dispersion produced by sulphate of quinine, and the other liquids above mentioned, is due *to a change of refrangibility in the rays of light.* The following experiment renders this evident:—

A solar spectrum is formed by means of an achromatic lens, and one or more prisms of flint glass, sufficiently pure to render visible the principal fixed lines, and a tube filled with a solution of sulphate of quinine is passed along this spectrum, from the red towards the violet end. Nothing peculiar is observed while the tube is held in the less refrangible part of the spectrum, the light passing through it freely and without sensible modification; but just before it reaches the extremity of the violet, a peculiar blue diffused light makes its appearance at the surface of the fluid by which the light enters, and remains visible even after the tube has passed beyond the violet into the invisible portion of the spectrum, acquiring in fact its greatest intensity at a certain distance beyond the extreme violet.

* Phil. Trans. 1852, ii. 463.

The stratum of liquid from which the diffused blue light emanates is thinner in proportion as the incident rays are more refrangible; and, from a little beyond the extreme violet to the end of the spectrum, the blue space is reduced to an excessively thin stratum adjacent to the surface by which the rays enter. It appears, therefore, that the solution, though transparent with respect to nearly the whole of the visible rays, is of an inky blackness with respect to the invisible rays more refrangible than the violet. Nevertheless, these rays, when once they have been converted into the visible blue light, pass through the liquid with facility. They must, therefore, be essentially altered in character. Now a change in the quality of light must consist, either in a modification of its state of polarisation, or in its period of undulation. The former supposition is excluded by the fact that the light thus modified is not polarised at all. It must, therefore, have undergone a change in its rate of vibration, and consequently a change of refrangibility. The existence of this change is, moreover, distinctly proved by examining the diffused light with a prism. It is then found to be by no means homogeneous, but to be resolvable into rays of unequal refrangibility, the whole of which are however comprised within the limits of the visible spectrum. *The diffused blue light consists of the chemical rays rendered visible by a change in their refrangibility.*

The diffusion thus produced is entirely distinct from that which is due to reflection from irregularities or suspended particles. The two phenomena are often produced together in the same medium; but they are easily distinguished by the fact that the light diffused by irregular reflection is more or less polarised, whereas the light diffused in the manner above described is entirely unpolarised, even if the incident rays were themselves polarised. This phenomenon, to which Professor Stokes originally gave the name of *true diffusion*, to distinguish it from the false diffusion produced by irregular reflection, is now called FLUORESCENCE.

It is exhibited by many solutions, and by many solid bodies, opaque as well as transparent, the colour of the diffused light varying with the nature of the medium. An aqueous infusion of horse-chestnut bark exhibits it very strongly, producing the same blue colour as sulphate of quinine. Many compounds of sesquioxide of uranium are also highly fluorescent, and diffuse a greenish-blue light, especially the nitrate, and *canary-glass* (ii. 256). A decoction of madder mixed with alum gives a yellow or orange-yellow fluorescence; tincture of turmeric and alcoholic extract of thorn-apple seeds diffuse a greenish light; an alcoholic solution of chlorophyll, a red light.

When the fluorescence is strong, as with sulphate of quinine, it may be seen by merely viewing the substance by ordinary diffused daylight. For more accurate observation, and for detecting fluorescence when it exists only in a slight degree, the following method is recommended by Professor Stokes*:—

Light is admitted into a darkened room through a hole several inches in diameter in the window shutter, and the object to be examined is placed on a small shelf, blackened at the top, and fixed just below. The hole is covered with an absorbing medium, called the *principal absorbent*, so selected as to transmit only the feebly luminous and invisible rays of high refrangibility. The body on the shelf is viewed through the second medium, the *complementary absorbent*, which is chosen so as to be as transparent as possible to those rays which are absorbed by the first, and to absorb all the rays which are transmitted by the first. If the media are well selected, they produce a very near approach to perfect darkness; and if the object appears unduly luminous, that effect most probably arises from fluorescence. To determine whether the illumination is really due to that cause, the complementary absorbent is removed from before the eyes to the front of the aperture, when the illumination, if really due to fluorescence,

* Phil. Mag. [4], vi. 304.

almost wholly disappears; whereas, if it be due merely to scattered light capable of passing through both media, it remains. In examining feebly fluorescent substances, however, it is better to keep the second medium in its place before the eye, and to use a third medium, the *transfer-medium*, placing the last alternately in the path of the incident rays, and between the object and the eye. Still greater delicacy of observation is attained by placing the substance side by side with a small white porcelain tablet, which is quite destitute of fluorescence, and examining the two as above. Or, again, the object being placed on the tablet, a slit is held close to it, in such a position as to be seen projected, partly on the object, partly on the tablet, and the slit is viewed through a prism. The fluorescence of the object is evidenced by light appearing in regions of the spectrum, in which the rays coming through the principal absorbent, and scattered by the tablet, produce nothing but darkness. These methods are delicate enough to show the fluorescence of white paper, even on a very gloomy day.

It is not merely the most refrangible rays that are capable of producing fluorescence; the rays of any part of the spectrum may undergo this change. By examining different media with the spectrum in the manner already described, it is seen that the fluorescence begins, sometimes in the blue, sometimes in the yellow. With an alcoholic solution of chlorophyll, it begins in the red. But wherever the change of refrangibility may begin, it is always in one direction, consisting in a diminution of the index of refraction, and a consequent depression of the light in the scale of colours. In other words, the *length of the wave is increased, and its velocity of undulation diminished.* The vibrations of the ether in the incident ray appear to excite disturbances within the complex molecules of the fluorescent medium, whereby new vibrations are excited in the ether, differing in period from those of the incident ray. The portion of the light which has produced

this molecular disturbance is used up, or *absorbed*, and thereby lost to visual perception, just as heat is converted into mechanical work. It is probable that the absorption of light always takes place in this manner. The well-known fact of the conversion of luminous rays into invisible calorific rays, is a striking instance of diminution of refrangibility accompanied by absorption.

As the most refrangible rays are the most active in producing fluorescence, it is natural that this effect should be most strikingly exhibited by the light of flames which are rich in those rays, — the flame of alcohol and of sulphur, for example. These flames do, in fact, produce the effect in a higher degree even than sunlight. An extremely beautiful effect is produced by exposing a number of highly fluorescent media, such as sulphate of quinine, infusion of horse-chestnut bark, and canary-glass, to the flame of sulphur burning in oxygen in a dark room.

The similarity of the blue light diffused by most fluorescent media to the phosphorescence exhibited by certain bodies, might lead us to suppose that the two phenomena proceed from the same cause. Such, however, is not the case: for fluorescence is entirely dependent on the incidence of certain rays, whereas phosphorescence is not; and, moreover, there is no apparent connection between fluorescent and phosphorescent bodies. So far as observation has yet gone, phosphorescent bodies are not fluorescent.

SPECTRA EXHIBITED BY COLOURED MEDIA.

The colour of an object depends upon the rays which it reflects or transmits to the eye; it is, in fact, the mixture or resultant of all the rays which the body does not absorb. We cannot, however, from observation with the unassisted eye, judge with certainty of the rays which are transmitted or reflected; because the same, or nearly the same, com-

pound tint may result from the union of very different primary colours. Thus a body may exhibit an indigo or violet tint, either because it absorbs all the rays excepting those which form the indigo or violet portions of the spectrum, or because it reflects or transmits the red and blue rays in certain proportions; similarly, a green colour may be the pure green of the spectrum, or a mixture of yellow and blue. In such cases, examination with the prism will show of what primary rays the colour is composed, and may thus afford the means of distinguishing between substances which, to ordinary observation, appear of the same colour.

Dr. Gladstone, who has lately made some very interesting observations on the absorption of light by coloured liquids *, introduces the liquid into a wedge-shaped vessel placed before a slit in the window-shutter of a darkened room, so that the line of light may be seen through various thicknesses of the liquid, from the thinnest possible film to a stratum perhaps three-quarters of an inch thick, and examines this line of coloured light with a prism held with its refracting angle parallel to the line of light. The whitish portion of the line, where the light traverses but a thin film of the liquid, is thereby expanded into a spectrum differing but little from that which is given by unaltered daylight; but as the line of light is viewed through deeper portions of the liquid, some rays are seen to diminish in intensity, others gradually to die out, while others almost immediately disappear, giving place to perfect darkness. With a good prism, on a tolerably clear day, the most conspicuous of Fraunhofer's lines may be seen. The appearances presented may be understood from the following representations of the effects produced by solutions of sesquichloride of chromium (Fig. 38) and permanganate of potash (Fig. 39).†

* Chem. Soc. Qu. J. x. 79.

† For representations of the spectra exhibited by a considerable number of coloured liquids, see Dr. Gladstone's paper above referred to.

The right-hand side of these figures corresponds with the red extremity of the spectrum: the letters refer to Fraunhofer's lines.

Fig. 38.

Fig. 39.

A comparison of the spectra exhibited by different salts, only one constituent of which is coloured, shows that, with very few exceptions, all the compounds of the same base or acid have the same effect on the rays of light. This law is seen to hold good in many instances which at first sight appear exceptional. Thus it is well known that some salts of chromic oxide are green, others red or purple. Now these differently-coloured chromic salts all exhibit the same general form of spectrum (Fig. 38), in which the violet and indigo rays are very soon cut off; and as the thickness increases, the light is more and more concentrated about two points, one in the red, the other in the bluish green, the red ray penetrating with the greatest facility. Hence it is that the chloride and other salts of chromium, which are green in moderately dilute solutions, appear purple or red when we look through a strong or very deep solution. The acetate absorbs the green rays more readily, and therefore appears green only in very weak solutions, or in thin strata, while the "red potassio-oxalate" absorbs the green so speedily that the thinnest portion of it appears bluish red.

Salts composed of a coloured base and a coloured acid exhibit colours compounded of the rays which are not absorbed by either, the resultant colour bearing, in many instances, but little resemblance to the original colours. Thus, the acid chromate of chromic oxide, a compound of two substances which give respectively yellow and green solutions, is not bright green, but brownish-red, because the chromic acid cuts off nearly all the blue and violet rays, while the oxide of chromium absorbs the yellow and the greater part of the green.

Some salts, which are but slightly coloured, nevertheless exhibit very characteristic spectra. Thus, a solution of sulphate of didymium, which has but a faint rose colour, exhibits, when examined by the hollow wedge and prism, a spectrum containing two very black lines, one in the yellow, the other in the green. These lines are visible in very weak solutions of didymium, and therefore serve as a delicate test for that metal; they moreover afford the means of distinguishing it from cerium and lanthanum, in the spectra of which they do not occur.

MEASUREMENT OF THE CHEMICAL ACTION OF LIGHT.

Chlorine and hydrogen combine under the influence of light, and form hydrochloric acid. Moreover, if the gaseous mixture is in contact with water, the resulting hydrochloric acid is immediately absorbed, and the diminution of volume thus produced affords a measure of the amount of chemical action. This mode of measurement was first adopted by Dr. Draper, of New York, whose experiments led to the important conclusion that *the chemical action of light varies in direct proportion to the intensity of the light, and to the time of exposure.*

But to give to this method all the exactness of which it is susceptible, certain conditions require to be fulfilled; the chief of which are perfect uniformity in the gaseous mixture,

constancy of pressure on the gas and liquids throughout the apparatus, and elimination of the disturbing action of radiant heat. These and other essential conditions are completely fulfilled in the apparatus used by Professor Bunsen and Dr. H. Roscoe in their late elaborate researches on the chemical action of light.*

This apparatus is represented in figure 40. To furnish the mixture of chlorine and hydrogen gases required, hydrochloric acid is decomposed in the glass vessel *a*, containing two carbon poles, connected by platinum wires with the four-celled Bunsen's battery, C. Between the battery and this vessel is interposed an instrument called the gyrotrope, by means of which the current may be made to pass either directly through the acid vessel *a*, or previously through the vessel *d* containing very slightly acidulated water, whereby the current is greatly weakened, and the evolution of gas in the vessel *a* reduced to a small amount. The mixture of chlorine and hydrogen passes from the vessel *a* through the washing-tube *w*, containing water, then forward through a horizontal tube provided with a glass cock, *h*, into the insolation vessel *i*, where the gases are exposed to the action of light. The lower part of this vessel, containing water, is blackened to protect it from the action of the light. From the insolation vessel, the gas passes through the horizontal measuring-tube K, provided with a millimeter scale, then through the water in the small vessel *l*, and finally into a vessel filled with fragments of charcoal and hydrate of lime, to absorb the excess of chlorine

When the gas is made to stream through the apparatus, the liquids in *a*, *w*, *i*, and *l*, become gradually saturated with gas; and as the saturation goes on, the composition of the gas varies. At length, however, after the stream of gas has been continued for three or four days, the liquids become saturated, and then the evolved gas is found to consist of exactly equal volumes

* Pogg. Ann. c. 43, 481 ; abstr. Proceedings of the Royal Society, viii. 235, 236, 516.

of chlorine and hydrogen. This normal state having been attained, the apparatus is ready for use, and retains its constant sensibility for weeks, requiring only a short saturation each day, previous to the actual observations.

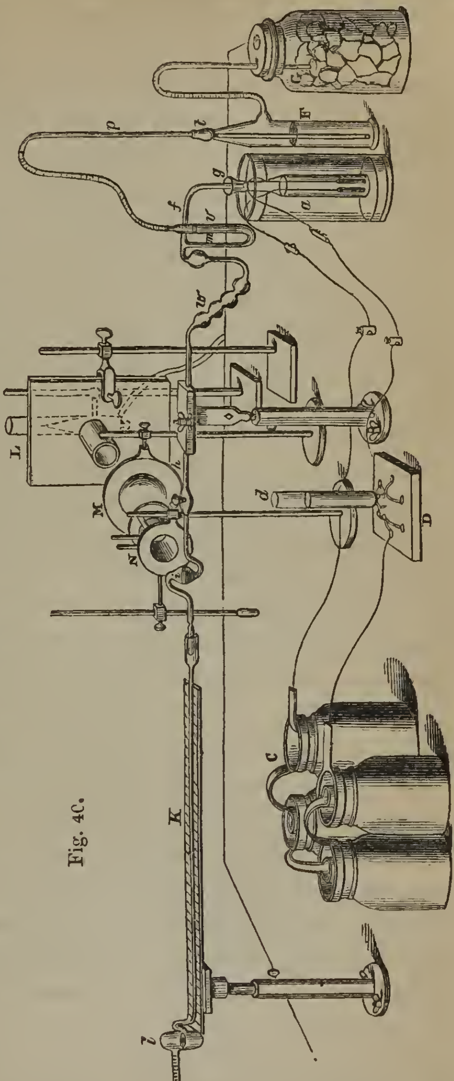


Fig. 40.

To make an observation, the stop-cock *h* is closed, and the light allowed to act on the gas in the upper part of the vessel *i*. Combination then takes place, accompanied by diminution of volume, and the external pressure forces the water in *l* through the tube K towards *i*. The position of the end of the column in the scale measures the diminution of volume.

The pressure on the gas in the insolation vessel and the measuring-tube during the observations, is necessarily uniform from the construction of the apparatus; but it is further necessary that uniformity of pressure be ensured in all parts of the apparatus

in the intervals between the observations; otherwise the composition of the gaseous mixture will be altered, and the results will no longer be exact. To ensure this uniformity of pressure, the gas, after the stopcock *h* is closed, is made to pass through the bent tube *m v v*, containing water, and thence through the tube *p*, which dips under the water in the vessel F, the pressure being regulated by raising or depressing this tube through the caoutchouc mouthpiece *t*. From the vessel F the gas is conveyed by a flexible tube into the condensing vessel G, containing charcoal and hydrate of lime. As soon as the stopcock *h* is closed, the gyrotrope wire is turned, so as to cause the current to pass through the vessel *d*, and thereby slacken the evolution of gas. When the stopcock *h* is open, the gas will pass one way or the other, according to the depth at which the tube *p* is immersed below the water in F.

To prevent any disturbance from the effects of radiant heat, the light from a coal gas flame, or other source, after being condensed by the convex lens *m*, is made to pass through the cylinder *n*, closed with plate-glass ends, and filled with water. A screen is placed in front of the insolation vessel, to prevent radiation of heat from the body of the observer; and this, together with the screen L, serves also to prevent radiation from external objects. The heat evolved in the insolation vessel by the combustion of the mixed gases, was found by direct experiment, not to exert any sensible influence on the results. All the parts of the apparatus between *a* and *l* are connected by ground-glass joints or by fusing; no caoutchouc, or any other organic matter, which could be acted upon by the chlorine, being introduced, excepting in those parts which merely serve to carry away the waste gas.

Photo-chemical Induction.—On exposing the gas to the light, the quantity of hydrochloric acid formed does not at once attain the maximum: a certain time always elapses before any

alteration of volume is perceptible; a slight alteration is, however, soon observed, and this gradually increases till the permanent maximum is reached. This remarkable fact was first observed by Draper, who explained it by supposing that the chlorine underwent, by exposure to light, a permanent allotropic modification, in which it possessed more than usually active properties. But Bunsen and Roscoe have shown that neither chlorine nor hydrogen, when separately insolated, undergoes any such modification, no difference being indeed perceptible between the action of light on a mixture of the gases which have been separately insolated before mixing, and on a mixture of the same gases evolved and previously kept in the dark. The light appears then to act by increasing the attraction between the chemically active molecules, or by overcoming certain resistances which oppose their combination. This peculiar action is called photo-chemical induction.

The time which elapses from the beginning of the exposure till the maximum action is attained, varies considerably according to circumstances, the maximum being sometimes reached in fifteen minutes, sometimes in three or four minutes. In one instance, the first action was visible only after six minutes' insolation, whilst in some experiments a considerable action was observed in the first minute.

The duration of the inductive action varies with the mass of the gas, and with the amount of light. With a constant quantity of light, it increases with the volume of the exposed gas. With a constant volume of gas it is found:—1. That the time necessary to effect the first action decreases with increase of light, and in a greater ratio than the increase of light.—2. That the time which elapses until the maximum is attained, also decreases with increase of light, but in a less ratio.—3. That the increase of the induction proceeds at first in an expanding series, and then converges till the true maximum is attained.

The condition of increased combining power into which the mixture of chlorine and hydrogen is brought by the action of

light, is not permanent; on the contrary, the resistance to combination overcome by the influence of the light, is soon restored when the gas is allowed to stand in the dark.

The resistance to combination which prevents the union of the gases until the action is assisted by light, may be increased by various circumstances, especially by the presence of foreign gases, even in very small quantity. An excess of $\frac{3}{1000}$ of hydrogen above that contained in the normal mixture, reduces the action from 100 to 38. Oxygen, in quantity amounting to only $\frac{5}{1000}$ of the total volume of gas, diminishes the action from 100 to 4·7; and $\frac{13}{1000}$ reduces it from 100 to 1·3. An excess of $\frac{10}{1000}$ of chlorine reduces the action from 100 to 60·2; and $\frac{180}{1000}$ from 100 to 41·3. A small quantity of hydrochloric acid gas does not produce any appreciable diminution; $\frac{6}{1000}$ of the non-insolated mixture reduces the action from 100 to 55.

The increase in the rate at which combination goes on up to a certain point under the influence of light, appears to arise, not from any peculiar property of light, but rather from the mode of action of chemical affinity itself. Chemical induction is in fact observed in cases in which there is nothing but pure chemical action to produce the alteration. Thus, when a dilute aqueous solution of bromine mixed with tartaric acid is left in the dark, hydrobromic acid is formed; and, by determining the amount of free bromine present in the liquid at different times, it is found that the rate at which the production of hydrobromic acid goes on is not uniform, but increases up to a certain point, according to a law similar to that which is observed in photo-chemical induction.

These phenomena seem to point to the conclusion that the affinity between any two bodies is in itself a force of constant amount, but that its action is liable to be modified by opposing forces, similar to those which affect the conduction of heat or electricity, or the distribution of magnetism in steel. We overcome these resistances when we accelerate the formation of a precipitate by agitation, or a decomposition by insolation.

Optical and Chemical Extinction of the Chemical Rays.—When light passes through any medium, part of it is lost by reflection at the surface, another portion by absorption within the medium, so that the quantity of emergent light is only a fraction of the incident light. This is true with regard to the chemical as well as to the luminous rays. By passing light from a constant source through cylinders with plate-glass ends filled with dry chlorine, it is found that, with a given length of cylinder, the quantity of the chemical rays transmitted, when no chemical action takes place, is to the quantity in the incident light in a constant ratio; in other words, the absorption of the chemical rays is proportional to the intensity of the light. It is also found that the quantity of chemical rays transmitted varies proportionally to the density of the absorbing medium.

But further, when light passes through a medium in which it excites chemical action, it is found that, in addition to the optical extinction already spoken of, a quantity of light is lost proportional to the amount of chemical action produced. The depth of pure chlorine at 0° C. and 0·76 mm. pressure, through which the light of a coal-gas flame must pass in order to be reduced to $\frac{1}{10}$, is found to be 173·3 millimeters. Hence, since the quantity of light absorbed varies as the density, the depth of chlorine diluted with an equal volume of air, or other chemically inactive gas, required to produce the same amount of extinction, would be 346·6 mm. But when the sensitive mixture of equal volumes of chlorine and hydrogen is used, the depth of the mixture which the light must penetrate to be reduced to $\frac{1}{10}$, is found to be only 234 mm. Hence, it appears that *light is absorbed in doing chemical work.*

With light from other sources, results are obtained similar in character, but differing in amount. Diffuse morning light reflected from the zenith of a cloudless sky is reduced to $\frac{1}{10}$ by passing through 45·6 mm. of chlorine, and through 73·5 mm. of the sensitive mixture; diffuse evening light is reduced to $\frac{1}{10}$ by passing through 19·7 mm. of chlorine and through

57·4 mm. of the standard mixture. Hence it appears that the chemical rays of diffuse morning light are absorbed by chlorine much more quickly than those of lamp-light; and those of evening light with still greater facility. From this we may conclude that the chemical rays reflected at different times and hours, possess, not only quantitative but also qualitative differences, similar to the various coloured rays of the visible spectrum. It is a fact well known to photographers, that the amount of light photometrically estimated gives no measure of the time in which a given photochemical effect is produced. For the taking of pictures, a less intense morning light is always preferred to a bright evening light.

ELECTRICITY.

Measurement of the Force of Electric Currents.—There are two methods by which the forces of electric currents are compared with each other, viz., the *chemical* or *electrolytic*, and the *electromagnetic methods.*

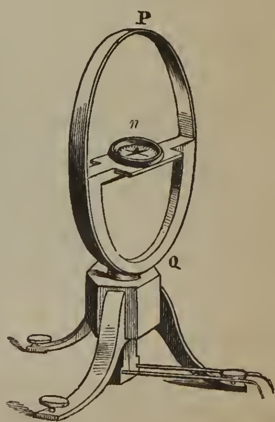
Faraday has shown that the amount of chemical work done is the same in all parts of the circuit; that, if two decomposing cells be introduced, one containing dilute sulphuric, the other hydrochloric acid, the quantity of hydrogen evolved is the same in both, and equal to the hydrogen evolved (by true current action) in each cell of the battery; moreover, that the quantities of different elements eliminated in any part of the circuit, are always in the ratio of their equivalent weights. The voltameter (I. 290) affords, therefore, a true and exact measure of the amount of the chemical or electrical force developed by the battery. But its indications are not always sufficiently rapid. In fact, in using this instrument, it is necessary to wait till a measurable quantity of gas is collected. It will, therefore, indicate the relative quantity of electricity

which has passed through the circuit in a certain finite interval, say in a minute; but it gives no information of any variations that may have taken place during that interval; moreover, it can only be used to measure currents of considerable strength.

The Tangent-compass.—To supply these deficiencies, and obtain exact and instantaneous indications of the relative forces of electric currents, recourse is had to the electro-magnetic method, which consists in observing the deflection of a magnetic needle produced by the current. Instruments for this purpose are called *Galvanometers* or *Rheometers.* The effect of a coil of wire in intensifying the effect of the current upon a magnetic needle, is described at page 290. Vol. I., of this work. But the kind of instrument there described, though commonly called a galvanometer, is really only a galvanoscope, or multiplier. It indicates with great delicacy the existence and direction of an electric current, but it is not constructed for quantitative determinations.

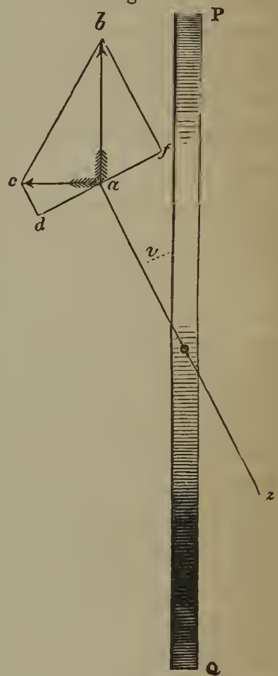
In the true galvanometer (Fig. 41) the current, instead of passing through a long coil of wire placed close to the needle, is made to pass through a broad circular band of brass or copper, P Q, of considerable dimensions, in the centre of which is placed a magnetic needle, *n*, the length of which is very small in comparison with the diameter of the circular conductor, so that the distance of the extremity of the needle from the conductor P Q, and consequently the force exerted upon it by the current, is sensibly the same at all angles of deflection. The instrument

Fig. 41.



is so placed that *the plane of the circle* P Q *coincides with the magnetic meridian.* To determine the relation which exists under these circumstances between the deflection of the needle and the force of the current, let P Q (Fig. 42) represent the circular conductor seen from above; $a\,z$ the direction of the needle under the influence of the current. The extremity of the needle is then acted upon by two forces, viz., the force of terrestrial magnetism acting parallel to P Q, and the force of the current acting at right angles to that direction. Let these forces be represented in magnitude and direction by the lines $a\,b$, $a\,c$. Draw also the line $f\,a\,d$ perpendicular to $a\,z$, and $b\,f$, $c\,d$, perpendicular to $d\,f$. Then the lines $a\,f$, $a\,d$ represent the resolved portions of the forces $a\,b$, $a\,c$, which act at right angles to the needle, and tend to turn it one way or the other. In order, therefore, that the needle may be at rest, $a\,d$ must be equal to $a\,f$, or

Fig. 42.



$$a\,c\,.\,\cos\ c\,a\,d = a\,b,\ \sin\ a\,b\,f.$$

Now the angle $c\,a\,d$ is equal to v, the angle of deflection of the needle from the meridian, because $a\,c$ is perpendicular to P Q, and $a\,d$ to $a\,z$; and the angle $a\,b\,f$ is also equal to v, because $a\,b$ is parallel to P Q, and $b\,f$ to $a\,z$. Hence the preceding equation becomes

$$a\,c\,.\,\cos\,v = a\,b\,.\,\sin\,v\,;$$

therefore

$$a\,c = a\,b\,.\,\tan\,v.$$

Or, if we denote the force of the earth's magnetism by M, and that of the electric current by E, we have

$$E = M\,\tan\,v.$$

Consequently, since the magnetic force of the earth is constant at the same place (at least for short intervals of time), *the magnetic force of the current is proportional to the tangent of the angle of deflection:* hence the name of the instrument.

Comparison between the chemical and magnetic actions of the current.—By introducing into the same voltaic curcuit, a voltameter and a tangent-compass, it is found that the *chemical action of the current is directly proportional to its magnetic action.* The tangent-compass affords, therefore, a measure of the chemical as well as of the magnetic force of the current, the quantity of chemical or electrical force in the circuit being proportional to the tangent of the angle of deflection of the needle.

If m milligrammes of hydrogen are evolved in a second in the voltameter, when the galvanometer exhibits a deflection of 45°, and therefore a current force = 1 (since $\tan 45° = 1$), then, when the same galvanometer shows a deflection = α, the quantity of hydrogen evolved in t seconds will be $m \,.\, t \,.\, \tan \alpha$. The quantity of any other element eliminated in the same circuit, will be found by multiplying this quantity by the equivalent weight of that element.

With a tangent-compass, the diameter of whose conductor measures one decimeter, it is found that, when the deflection is 45°, one milligramme, or 11·2 cubic centimeters (at 0° C. and Bar. 0·76 met.) of hydrogen is eliminated in 32·3 seconds. Hence with any other circular current whose radius is r decimeters and force = $\tan \alpha$, the time t in which 1 milligramme of hydrogen is evolved, or 9 milligrammes of water are decomposed, is

$$t = \frac{32{\cdot}3}{r \,.\, \tan \alpha}$$

Ohm's Formulæ.—The amount of electrical or chemical power developed in the voltaic circuit,—or, in other words,

the quantity of electricity which passes through a transverse section of the circuit, in a unit of time, evidently depends upon two conditions; viz., the power, or electromotive force of the battery, and the resistance offered to the passage of the current by the conductors, liquid or solid, which it has to traverse. With a given amount of resistance, the power of the battery is proportional to the quantity of electricity developed in a given time; and by a double or treble resistance, we mean simply that which, with a given amount of exciting power in the battery, reduces the quantity of electricity developed, or work done, to one-half or one-third. If, then, we denote the electromotive force of the battery by E, and the resistance by R, we have, for the quantity of electricity passing through the circuit in a unit of time, the expression:

$$q = \frac{E}{R} \cdot \cdot \cdot \cdot \cdot (1)$$

This is called Ohm's law, from the name of the distinguished mathematician who first announced it. It must be understood, not as a theorem, but as a definition. To say that the strength of the current varies directly as the electromotive force, and inversely as the resistance, is simply to define what we mean by electromotive force and what we mean by resistance.*

Let us now endeavour, by means of the formula (1), to estimate the effect produced on the strength of the current by increasing the number and size of the plates of the battery. The resistance R consists of two parts; viz. that which the current experiences in passing through the cells of the battery itself, and that which is offered by the external conductor which joins the poles. This conductor may consist either wholly of metal, or partly of metal and partly of electrolytic liquids.

* It must be remembered that we are here merely comparing the strength of electric currents one with the other, not reducing the current force to absolute mechanical measure, or even comparing it with the electro-static forces of attraction and repulsion. (See page 506.)

Let the resistance within the battery be r, and the external resistance r'; then, in the one-celled battery, we have

$$q = \frac{E}{r + r'} \quad \ldots \ldots \ldots (2)$$

Now suppose the battery to consist of n cells perfectly similar; then the electromotive force becomes nE, the resistance within the battery nr; if, then, the external resistance remains the same, the strength of the current will be denoted by

$$q = \frac{nE}{nr + r'} = \frac{E}{r + \frac{r'}{n}}, \quad \ldots \ldots \ldots (3)$$

If r' be small, this expression has nearly the same value as $\frac{E}{r + r'}$; that is to say, if the circuit be closed by a good conductor, such as a short thick wire, the quantity of electricity developed by the compound battery of n cells, is sensibly the same as that evolved by a single cell of the same dimensions. But if r' is of considerable amount, as when the circuit is closed by a long thin wire, or when an electrolyte is interposed, the strength of the current increases considerably with the number of plates. In fact, the expression (3) is always greater than (2); for—

$$\frac{nE}{nr + r'} - \frac{E}{r + r'} = \frac{(n - 1)\,Er'}{(nr + r')(r + r')};$$

a quantity which is necessarily positive when n is greater than unity.

Suppose, in the next place, that the size of the plates is increased, while their number remains the same. Then, according to the chemical theory, an increase in the surface of metal acted upon must produce a proportionate increase in the quantity of electricity developed, provided the conducting power of the circuit is sufficient to give it passage. According to the theory which attributes the development of the elec-

tricity to the contact of dissimilar metals, an increase in the size of the plates does not increase the electromotive force, but it diminishes the resistance within the cells of the battery by offering a wider passage to the electricity. Hence in the single cell, if the surface of the plates, and therefore the transverse section of the liquid, be increased m times, the expression for the strength of the current becomes

$$\frac{E}{\frac{r}{m} + r'} = \frac{m\,E}{r + m\,r'}.$$

If r' be small, this expression is nearly the same as $\frac{m\,E}{r + r'}$, that is to say, the quantity of electricity in the current increases very nearly in the same ratio as the size of the plates; but when the external resistance is considerable, the advantage gained by increasing the size of the plates is much less.

We may conclude, then, that when the resistance in the circuit is small, as in electro-magnetic experiments, a small number of large plates is the most advantageous form of battery; but in overcoming great resistances, power is gained by increasing the number rather than the size of the plates.

Electric Resistance of Metals.—The preceding principles enable us to determine the manner in which the resistance of a metallic wire varies with its length. For this purpose suppose a one-celled battery (Daniell's) to be used, which maintains a constant action during the time of the experiment. First let the current be made to pass directly through the tangent-compass, and afterwards let wires, of uniform thickness and of the lengths of 5, 10, 40, 70, and 100 meters, be interposed in the circuit, and the resulting deflections observed. Now, as the force of the battery is constant, the resistance is inversely as the strength of the current. But the total resistance is made up of that of the interposed wires, together with that of the battery itself, and that of the conductor of the tangent-compass. These last two resistances

we may suppose to be equal to that of a wire of the same thickness as the above, and of a certain unknown length, x. Instead, therefore, of the lengths of wire 5, 10, 40, &c., we must substitute $x + 5$, $x + 10$, $x + 40$, &c. An experiment of this kind* gave the following results:—

Length of Wire.	Observed Deflection.	Tangent of Deflection.
x meters	62° 0′	1·880
x + 5	40 20	0·849
x + 10	28 30	0 543
x + 40	9 45	0·172
x + 70	6 0	0·105
x + 100	4 15	0·074

Now, let us assume, as most probable, that the resistance of a wire increases in direct proportion to its length, then, according to Ohm's law, the first two experiments give:—

$$x : x + 5 = 0{\cdot}849 : 1{\cdot}880$$

whence, $x = 4{\cdot}11$. And, by combining in a similar manner the first experiment with all the others, we obtain for x the several values 4·06, 4·03, 4·14, 4·09, the mean of the whole being 4·08. Substituting this value for x in the preceding table, and calculating the corresponding deflections on the supposition that the strength of the current varies inversely as the resistance, that is as the length of the conductor, we obtain the following results:—

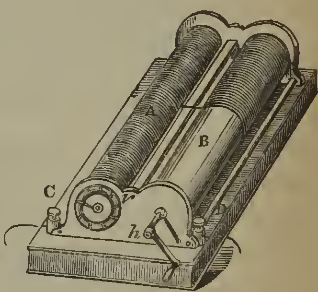
Length of Conductor.	Calculated Deflection.	Observed Deflection.	Difference.
4·08 meters	62° 0′	62° 0′	
9·08	40 18	40 20	+ 2′
14·08	28 41	28 30	− 11
44·08	9 56	9 45	− 11
74·08	5 57	6 0	+ 3
104·08	4 14	4 15	+ 1

* Müller, Lehrbuch der Physik. 1853, ii. 177.

From the results of this and similar experiments, it is inferred that—*the resistance of a conductor of uniform thickness varies directly as its length.*

The Rheostat or Current-regulator.—The various forms of the so-called constant battery, Daniell's for example (I. 284), attain their end but imperfectly, a galvanometer included in the circuit always exhibiting more or less variation. A really constant current can only be obtained by interposing in the circuit a conducting wire of variable length, so that the resistance may be increased or diminished as the action of the battery becomes stronger or weaker. Various instruments have been contrived for this purpose. The one most used, invented by Professor Wheatstone, is represented in fig. 43.

Fig. 43.



A and B are two cylinders of the same dimensions—the first of dry wood, the second of brass—placed with their axes parallel to each other. The wooden cylinder A has a fine screw cut on its surface, and around it, following the thread of the screw, is coiled a thin brass wire. One extremity of this wire is attached to a brass ring, *v*, at the nearer end of the wooden cylinder, and the other to the farther extremity of the brass cylinder. The ring *v* and the nearer end of the brass cylinder are connected with the wires of the battery through the medium of the screw-joints C D. A movable handle, *h*, serves to turn the cylinders alternately round their axes. By turning B to the right, the wire is uncoiled from A and coiled upon B; and the contrary when A is turned to the left. The number of coils of wire upon A are indicated by a scale placed between the cylinders, the fractions of a turn being measured by an index moving round the ring *v*, which is graduated accordingly. As the coils of the wire are insulated

on the wooden cylinder, but not on the brass, it is evident that the path of the current will be longer, and therefore the resistance greater, in proportion to the number of coils of wire upon the wooden cylinder.

By means of the rheostat and the tangent-compass, the resistances afforded by different conductors to the passage of the current may be measured with great facility. Suppose that when the wire of the rheostat is completely uncoiled from the wooden cylinder (the index then standing at 0°), a tangent-compass introduced into the circuit shows a deflection of 46°. Then let a copper wire four yards long and $\frac{1}{20}$th of an inch thick, be introduced into any part of the same circuit. The galvanometer-needle will then exhibit a smaller deflection, say 37°. On removing the wire, the galvanometer will again exhibit its former deflection of 46°. Now let the rheostat wire be coiled round the wooden cylinder till the needle returns to 37°, and suppose that to produce this effect twenty turns of the rheostat wire are necessary. This length of the rheostat wire produces a resistance equal to that of the wire under examination. Next let a similar experiment be made with a wire of the same length but of twice the thickness, and consequently having a transverse section four times as great as that of the former. It will be found that five turns of the rheostat wire, or one-fourth of the former length, are sufficient to produce a resistance equal to that of the second wire. By experiments thus conducted it is found that: *The resistance of a wire or any other conductor of given length varies inversely as its transverse section.* And comparing this result with that which was established at page 503, we find that: *Conductors of the same material offer equal resistances, when their lengths are to one another in the same proportion as their transverse sections.*

In a similar manner, the relative conducting powers of different metals may be ascertained. Taking the resistance of pure copper as the unit, it is found that that of iron is

7·02, of brass 3·95, of German silver 15·47. The conducting powers are of course inversely as these numbers (II. 441).

Heating Power of the Voltaic Current.—The degree of heat excited in a metallic wire by the passage of the current, increases with the strength of the current and with the resistance of the wire. To determine the numerical relations of this phenomenon, the wire to be heated is formed into a spiral and enclosed within a vessel containing strong alcohol, or some other non-conducting liquid, in order that the current may pass entirely through the wire, and not through the liquid itself. The rise of temperature in the liquid is noted by a delicate thermometer; the strength of the current measured by the tangent-compass; and the resistance of the wire afterwards determined in the manner above described. By this method Lenz* has shown that:—

The quantity of heat evolved in a given time is directly proportioned to the resistance of the wire, and to the square of the quantity of electricity which passes through it.

The same result has been obtained by Joule†, both for wires and liquid conductors; by E. Becquerel for liquids; and by Riess‡ for the heat produced by the discharge of the electricity accumulated in a Leyden jar.

Reduction of the Force of the Current to absolute mechanical Measure:—This important determination has been made the subject of an extensive research by Weber and Kohlrausch.§ To understand the results obtained by these philosophers, it is necessary to define exactly the several units of measurement adopted:

a. The unit of electric fluid is the quantity which, when concentrated in a point, and acting on an equal quantity of

* Pogg. Ann. lxi. 18.

† Phil. Mag. [3], xix. 210.

‡ Pogg. Ann. xl. 335; xliii. 47; xlv. 1.

§ Abhandlungen derMathematisch-physischen Classe der Königl. Sachsischen Gesellsch. d. Wiss. Leipzig. 1856.

the same fluid also concentrated in a point, and at the unit of distance, exerts a repulsion equal to the unit of force.

b. The unit of electrochemical intensity is the force of the current which, in a unit of time, decomposes a unit of weight of water, or an equivalent quantity of any other electrolyte.

c. The unit of electromagnetic force, is the force of a current which — when it traverses a circular conductor whose area is equal to the unit of surface, and acts upon a magnet whose magnetic moment is equal to unity, the magnet being placed at a great distance, and in such a manner that its axis is parallel to the plane of the conductor, and its centre on a line drawn through the centre of the circular conductor, and perpendicular to its plane — exerts upon the magnet a rotatory force equal to unity divided by the cube of the distance between the centre of the needle and the centre of the conductor.

Weber had shown by previous experiments that the unit of electrochemical force is to that of electromagnetic force as $106\frac{2}{3}$ to 1. It remained, therefore, to determine the relation between the electromagnetic unit and the electrostatic unit (1), and thus to establish a numerical relation between statical and dynamical electricity. The mode of experimenting was as follows: —

1. A Leyden jar having been strongly charged, its knob was touched with a large metallic ball, which took from it a certain portion of its charge, determined by previous experiments. The charge of the ball was then transferred to the torsion-balance, and the repulsive force measured. At the same time, the remainder of the charge of the jar was made to traverse the wire of a galvanometer, previously, however, having been passed through a long column of water, in order to give it a sensible duration, and prevent it from passing from one coil of the wire to another in the form of a spark. In this manner, a relation was established between the statical and dynamical effects of the charge of the jar. — 2. The

intensity and duration of a voltaic current were determined, which imparted to the galvanometer needle the same deflection as that produced by the discharge of the Leyden jar.

The results of the experiments were as follows:—

Through each section of a conductor traversed by a current whose force is equal to the electromagnetic unit, there passes in a second of time a quantity of positive electricity equal to $155,370 \times 10^6$ statical units (p. 506, *a*), and an equal quantity of negative electricity travelling in the opposite direction.

The quantity of electricity required to decompose one milligramme of water, amounts to $106\frac{2}{3}$ times this quantity, or $16,573 \times 10^9$ units of electricity, of each kind. To decompose nine milligrammes of water, or one equivalent, requires of course nine times this amount of electricity. This quantity of positive electricity $(9 \times 16,573 \times 10^9)$ accumulated on a cloud situated 1000 meters above the surface of the earth, and acting on an equal quantity of negative electricity on the surface of the earth below the cloud, would exert an attractive force equal to 226,800 kilogrammes, or 208 tons.

From the same data it is calculated that, if all the particles of hydrogen in one milligramme of water in the form of a column one millimeter long, were attached to a thread, and all the particles of oxygen to another thread, then, to effect the decomposition of the water in a second, the two threads would require to be drawn in opposite directions, each with a force of 147,380 kilogrammes, or 145 tons. If the water were decomposed with less velocity, the tension would be proportionally less.

CHEMICAL NOTATION AND CLASSIFICATION.

ATOMS AND EQUIVALENTS.

EQUIVALENT quantities of any two substances are such as can replace one another in combination, producing compounds of similar chemical character. Thus, when copper is immersed in a solution of nitrate of silver, 31·7 parts of copper take the place of 108 parts of silver, forming a neutral nitrate of copper. Similarly, the 31·7 parts of copper may be replaced by 32·5 parts of zinc, and these again by 39 parts of potassium, the product of the substitution being in each case a neutral salt. These quantities of silver, copper, zinc, and potassium, are therefore equivalent to one another: they discharge analogous chemical functions. In like manner, 47 parts of potash, and 31 parts of soda are equivalent, because they unite with the same quantity of an acid to form neutral salts.

Equivalent numbers cannot, however, be always determined by actual substitution. Six parts of carbon are said to be equivalent to 14 parts of nitrogen; but there is no known instance of the direct replacement of nitrogen by carbon. Moreover, certain quantities of sulphuric acid and soda are spoken of as equivalent to one another, although it is plainly impossible that bodies so opposite in character should discharge the same chemical function. In fact, the term equivalent is frequently used, not in its strict etymological sense, but as synonymous with *combining number*. Eight parts of oxygen are said to be equivalent to 1 part of hydrogen, because the bodies unite in this proportion to form water (I. 123). This confusion of the terms equivalent and combining number,

arises from the circumstance that the combining numbers in most general use have been selected so as to represent, in many cases, the true equivalents. Nevertheless, the ideas of equivalent and combining proportion are essentially different, and the numbers which relate to them cannot be made to coincide in all cases. The numbers which represent the proportions in which bodies combine, though to a certain extent arbitrary, may be regarded as fixed when once selected; but the equivalent of a body varies according to the chemical function which it discharges. When iron dissolves in hydrochloric acid, producing ferrous chloride, FeCl, every grain of hydrogen expelled from the acid is replaced by 28 grains of iron; but when the same metal dissolves in *aqua regia*, forming ferric chloride, Fe_2Cl_3 or $Fe\frac{2}{3}Cl$, each grain of hydrogen in the acid is replaced by $18\frac{2}{3}$ grains of iron; in other words, the equivalent of iron ($H = 1$) is 28 in the ferrous acid, $18\frac{2}{3}$ in the ferric compounds. Similarly, the equivalent of mercury is 200 in the mercurous, 100 in the mercuric compounds. By comparing the perchlorates with the permanganates, it appears that 55·7 parts of manganese are equivalent to 35·5 parts of chlorine. Now this same quantity of chlorine is equivalent to 8 parts of oxygen, and to 16 parts of sulphur: moreover, the analogy of the sulphates and manganates shows that 16 parts of sulphur are equivalent to 27·7 parts of manganese, *i. e.* half the former quantity. Lastly, by comparing the manganous with the manganic salts, it appears that if the equivalent of manganese be 27·7 in the former, it must be 18·5 in the latter. Manganese has, therefore, three different equivalents, according to the kind of compound into which it enters; and, generally, the number of equivalents which may be assigned to a body is equal to the number of chemical functions which it discharges.

The so-called tables of equivalents are really, as already observed, tables of combining proportion. How are these combining proportions determined? Most bodies unite with

others in more than one proportion. Eight parts of oxygen combine with 14, 7, 4·7, 3·5, and 2·8 parts of nitrogen. Which of these numbers is to be taken as the combining number of nitrogen? Again,—1 part of hydrogen unites with $4\frac{2}{3}$ parts of nitrogen, and yet the combining number of nitrogen ($H = 1$), is said to be not $4\frac{2}{3}$, but three times that number, viz. 14. Why is this last number adopted? The solution of such questions leads to a variety of considerations. Obviously, the combining numbers should be so selected as to represent all series of compounds by the simplest formulæ, and to express analogous combinations by similar formulæ. Practically, however, this rule is not found to be a sufficient guide in all cases; and, in the actual determination of combining numbers, reference is constantly made to considerations intimately related to the atomic theory, such as isomorphism, the specific heat of atoms, vapour-densities, and the basicity of acids. Suppose, for example, the combining number of an acid is to be determined; the first thing to be ascertained is its saturating power. But then arises the question,—is the acid monobasic, bibasic, or tribasic? Now, on the system of combining numbers or equivalents, viewed without reference to atomic constitution, such a question has no meaning. Why, for example, is citric acid said to be tribasic? Because the formula of a neutral citrate is $C_{12}M_3O_{14}$; a formula which does not admit of division by 3, without introducing a fractional number of oxygen-atoms. But if the symbols merely denote combining numbers or equivalents, there can be no valid objection to the use of such fractional numbers. There is nothing absurd in the idea of $\frac{14}{3}$ of the quantity of oxygen which unites with one pound of hydrogen to form water. But if the symbols denote atoms, the case is altered, the idea of a divided atom being self-contradictory.

This is but one instance out of many of the influence exerted by the atomic theory on the construction of chemical formulæ, and consequently on the determination of combining numbers.

These numbers do, in fact, represent the supposed relative weights of atoms. Different views may be entertained of the atomic constitution of bodies; and, in the present state of chemical knowledge, the determinations of the atomic weight of a body from different points of view may not always agree: the specific heat, for example, sometimes leading to one conclusion, the vapour-density to another; but the idea of atoms and of their relative weights, and of the building up of compounds by the juxta-position of elementary atoms, is perfectly definite, and affords the only satisfactory explanation yet given of the observed laws of chemical combination (I. 135).

GERHARDT'S UNITARY SYSTEM.

There are three systems of atomic weight in use among chemists:—1. The system adopted in this work, which is the same as that in Gmelin's Hand-book. In this system, water is represented by the formula HO, and the metallic oxides (protoxides) most resembling it by the formula MO. The atomic weights correspond, for the most part, with the equivalents, substitution being supposed to take place, atom for atom.

2. The system of Berzelius, based upon the hypothesis that all elementary gases contain equal numbers of atoms in equal volumes, so that the atomic constitution of a compound corresponds with its constitution by volume. Thus, water being composed of 2 vol. H to 1 vol. O, is H_2O; hydrochloric acid, being composed of equal volumes of chlorine and hydrogen, is HCl, &c. The atomic weights in this system are the same as those in the former (I. 108), excepting those of hydrogen, nitrogen, phosphorus, chlorine, bromine, iodine, and fluorine, which have half the values there assigned to them, viz.:—(O = 8); H = 0·5; N = 7; P = 16·01; Cl = 17·75; I = 63·18; Br = 40; F = 9·35. Metallic

protoxides are represented by the formula MO: *e.g.* potash = KO; black oxide of copper = CuO.

3. The system of Gerhardt, based, like that of Berzelius, on the hypothesis that all simple gases contain equal numbers of atoms in equal volumes, but carrying out that system more consistently. The formula of water in Gerhardt's system is H_2O, as in that of Berzelius. Moreover, as the vapour-density of mercury is to that of oxygen as 6976 : 1106 (I. 149), and mercuric oxide contains 8 parts by weight of oxygen to 100 parts of mercury, it follows that the proportions by volume of mercury-vapour and oxygen which compose this oxide must be 2 vol. mercury to 1 vol. oxygen: for $2 \times 6976 : 1106 = 100 : 8$ (nearly). Hence mercuric oxide is Hg_2O; and from the analogy of cupric oxide, ferrous oxide, potash, soda, &c., with mercuric oxide, it follows that these oxides must be Cu_2O, Fe_2O, K_2O, Na_2O, &c.; or, generally, the formula of a protoxide is M_2O, analogous to that of water, H_2O.

If O = 8, the atomic weights of sulphur, selenium, tellurium, and carbon are the same in Gerhardt's system as in that adopted in the present work, but those of all the other elements have only half the usual values:—H = 0·5, Cl = 17·75, K = 19·5, &c. Or, what is more convenient, assuming H = 1, the atomic weights of O, S, Se, Te, and C will be doubled, while those of all the other elements will remain the same.*

In the following explanations and applications of Gerhardt's system, these double atomic weights of oxygen, &c., will, to avoid confusion, be denoted by letters with bars through the middle: thus, O̶ = 16, S̶ = 32, C̶ = 12.

The following table presents a comparative view of the

* Gmelin, in his Handbook (Translation, vol. vii. p. 27), objects to Gerhardt's atomic weights, that they do not correspond with the equivalent numbers; but this, as already shown (p. 510), must necessarily be the case with all systems of atomic weights or combining numbers, inasmuch as a body may have several equivalents, but can have only one atomic weight.

formulæ of some of the most important chemical compounds in the ordinary notation, and in that of Gerhardt.

	Ordinary System.	Gerhardt's System.
Water	HO	$H_2\Theta$
Peroxide of hydrogen . . .	HO_2	$H\Theta$
Hydrosulphuric acid . . .	HS	$H_2\cancel{S}$
Sulphuric acid (anhydrous) . .	SO_3	$\cancel{S}\Theta_3$
" " (hydrated) . .	SHO_4	$\cancel{S}H_2\Theta_4$
Hydrochloric acid	HCl	HCl
Hypochlorous acid (anhydrous) .	ClO	$Cl_2\Theta$
" " (hydrated) . .	$ClHO_2$	$ClH\Theta$
Carbonic oxide	CO	$\cancel{C}\Theta$
Carbonic acid (anhydrous) . .	CO_2	$\cancel{C}\Theta_2$
Nitric acid (anhydrous) . . .	NO_5	$N_2\Theta_5$
" " (hydrated) . . .	NHO_6	$NH\Theta_3$
Phosphoric acid (anhydrous) . .	PO_5	$P_2\Theta_5$
" " (hydrated) . .	PH_3O_8	$PH_3\Theta_4$
Protoxides (anhydrous) . . .	MO	$M_2\Theta$
" (hydrated) . . .	MHO_2 or $MO.HO$	$MH\Theta$
Sesquioxides (anhydrous) . .	M_2O_3	$M_4\Theta_3$
Sulphate of potash (neutral) . .	SKO_4	$\cancel{S}K_2\Theta_4$
" " (acid) . .	S_2KHO_8	$\cancel{S}KH\Theta_4$
Nitrate of potash	NKO_6	$NK\Theta_3$
Alum (anhydrous)	$S_4KAl_2O_{16}$	$\cancel{S}_2KAl_2\Theta_8$
Hydrocyanic acid	C_2NH	$\cancel{C}NH$
Cyanic acid	C_2NHO_2	$\cancel{C}NH\Theta$
Cyanate of soda	C_2NNaO_2	$\cancel{C}NNa\Theta$
Hydrosulphocyanic acid . . .	C_2NHS_2	$\cancel{C}NH\cancel{S}$
Sulphocyanide of silver . . .	C_2NAgS_2	$\cancel{C}NAg\cancel{S}$
Alcohol	$C_4H_6O_2$	$\cancel{C}_2H_6\Theta$
Ether	C_4H_5O	$\cancel{C}_4H_{10}\Theta$
Acetic acid (hydrated) . . .	$C_4H_4O_4$	$\cancel{C}_2H_4\Theta_2$
" " (anhydrous) . . .	$C_4H_3O_3$	$\cancel{C}_4H_6\Theta_3$
Benzoic acid (hydrated) . . .	$C_{14}H_6O_4$	$\cancel{C}_7H_6\Theta_2$
" " (anhydrous) . .	$C_{14}H_5O_3$	$\cancel{C}_{14}H_{10}\Theta_3$
Benzoate of potash	$C_{14}H_5KO_4$	$\cancel{C}_7H_5K\Theta_2$
Oxalic acid	$C_4H_2O_8$	$\cancel{C}_2H_2\Theta_4$

These two systems of notation possess in common the advantage of representing the metallic protoxides by formulæ analogous to that of water, whereas in the system of Berzelius, this analogy is lost, water being represented by $H_2\Theta$, and the protoxides of the metals by $M\Theta$. But the representation of water by $HH\Theta$, as in Gerhardt's system, possesses the additional advantage of corresponding with the

important fact, that it is possible to replace either the half or the whole of the hydrogen in water by a metal. Thus potassium thrown into water displaces half the hydrogen, and forms hydrate of potash, $HK\Theta$; and when this compound, in the solid state, is heated with an additional quantity of potassium, the remaining half of the hydrogen is displaced, and anhydrous potash, $KK\Theta$, is formed. On the contrary, when potassium acts on hydrochloric acid, HCl, it displaces the whole of the hydrogen, and forms chloride of potassium KCl. This is an important difference, which is easily understood on the supposition that water contains two atoms and hydrochloric acid only one atom of hydrogen; whereas, if these two compounds are represented by the analogous formulæ HO and HCl, the cause of the difference of action is by no means apparent.

Assuming as the unit of vapour-volume the space occupied by 1 gramme of hydrogen (or by 16 grammes of oxygen, 14 of nitrogen, 35·5 of chlorine, &c.), and calculating by formulæ analogous to those in the third column of the preceding table, the weights of the compound atoms or molecules of those compounds which are capable of assuming the gaseous form, it will be found that they correspond to 2 volumes of vapour. Thus, for hydrochloric acid: $H + Cl = 1 + 35{\cdot}5 = 36{\cdot}5$; and as the density of hydrochloric acid gas is 18·25 times that of hydrogen (see Table I. p. 150.), it follows, that the number 36·5 represents the weight of 2 volumes of vapour. Similarly, for water: $H_2\Theta = 2 + 16 = 18$, which is also the weight of 2 volumes of vapour, the specific gravity of aqueous vapour compared with hydrogen as the unit being 9. Alcohol $= C_2H_6\Theta = 24 + 6 + 16 = 46$: and the specific gravity of alcohol vapour $(H = 1)$ is 23. Ether $= C_4H_{10}\Theta = 48 + 10 + 16 = 74$, which is twice 37, the weight of a unit-volume of ether-vapour.

In the formulæ of the second column, this uniformity of vapour-volume is not observed. Some of them, as those of water HO, ether C_4H_5O, anhydrous acetic acid $C_4H_3O_3$, and

hydrated sulphuric acid SHO_4, represent 1 volume of vapour, when referred to the unit above-mentioned, viz. the space occupied by 1 gramme of hydrogen, or 2 volumes, if compared with the volume of half a gramme of hydrogen, or 8 grammes of oxygen; while the rest, for example, hydrochloric acid, HCl, and hydrated acetic acid, $C_4H_4O_4$, represent 2 volumes or 4 volumes of vapour, according to the unit adopted. (See the table in Vol. I., pp. 149-155.) To bring all these formulæ to the same standard of vapour-volume, it is necessary, therefore, to double those first mentioned, thus: water $= H_2O_2$; ether, $C_8H_{10}O_2$; anhydrous acetic acid, $C_8H_6O_6$; hydrated sulphuric acid, $S_2H_2O_8$, &c.; and if the corresponding change be made in the formulæ of the analogous compounds, which are not known to exist in the gaseous state, *e. g.* anhydrous metallic protoxides, M_2O_2; neutral sulphate of potash, $S_2K_2O_8$, &c., it will be found that Gerhardt's formulæ may, in all cases, be converted into those of the ordinary notation, by doubling the number of atoms of carbon, oxygen, sulphur, selenium, and tellurium.*

There is yet one class of bodies whose atomic weights represent, not two, but one volume of vapour, viz. the elementary bodies. To reduce these bodies to the same standard, it is necessary to assume that each molecule of an elementary body in the free state consists of two elementary atoms, *e. g.* hydrogen, HH; chlorine, ClCl.

This hypothesis is justified by numerous considerations. First: It accords with the polar view of the constitution of bodies suggested by the phenomena of electrolysis (I. 238). Secondly: It is justified by certain relations of boiling point

* Gerhardt applied the term *unitary* to his system of notation, because it is based on the reduction of all formulæ to one common standard, the formulæ being derived one from the other by substitution. The ordinary system, being founded rather on the formation of compounds in successive binary groups (*e. g.* potash = KO; sulphuric acid = SO_3; sulphate of potash = $KO.SO_3$), is called the *Dualistic system.*

and vapour-density, to be considered hereafter. Thirdly: There are numerous instances of chemical action in which two atoms of an elementary body unite together at the moment of chemical change, just like heterogeneous atoms. Thus, when the hydride of copper, Cu_2H, is decomposed by hydrochloric acid, cuprous chloride is formed, and a quantity of hydrogen evolved equal to twice that which is contained in the hydride itself:—

$$Cu_2H + HCl = Cu_2Cl + HH.$$

This action is analogous to that of hydrochloric acid on cuprous oxide:—

$$Cu_4\cancel{O} + 2HCl = 2Cu_2Cl + H_2\cancel{O}.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen; in the former, with hydrogen. When solutions of sulphurous and hydrosulphuric acids are mixed, the whole of the sulphur is precipitated:—

$$\cancel{S}\cancel{O}_2 + 2H_2\cancel{S} = 2H_2\cancel{O} + \cancel{S}\,.\,\cancel{S}_2,$$

the action being similar to that of sulphurous acid on hydroselenic acid:—

$$\cancel{S}\cancel{O}_2 + 2H_2\cancel{Se} = 2H_2\cancel{O} + \cancel{S}\,.\,\cancel{Se}_2.$$

In the one case, a sulphide of selenium is formed; in the other, a sulphide of sulphur. The precipitation of iodine which takes place on mixing hydriodic with iodic acid, affords a similar instance of the combination of homogeneous atoms. The reduction of certain metallic oxides by peroxide of hydrogen, is another striking example of this kind of action. When oxide of silver is thrown into this liquid, water is formed; the silver is reduced to the metallic state; and a quantity of oxygen is evolved equal to twice that which is contained in the oxide of silver. It appears, indeed, as if atoms could not exist in a state of isolation. An atom of an elementary body

must unite, either with an atom of another element, or with one of its own kind.

The same tendency of homogeneous atoms to combine together is exhibited by certain groups of atoms called compound radicals, which behave in most respects like elementary substances, and pass as entire groups from one state of combination to another. Thus there is a series of hydrocarbons called the *alcohol-radicals* (p. 531), *e.g.* methyl, CH_3; ethyl, C_2H_5, which may be regarded as compound metals, capable of taking the place of hydrogen in combination with chlorine, iodine, oxygen, &c., just as simple metals do. Now when zinc-ethyl, C_2H_5Zn, and iodide of methyl, CH_3I, are heated together, double decomposition takes place, the products being iodide of zinc, and methyl-ethyl:—

$$C_2H_5 . Zn + CH_3I = ZnI + (C_2H_5) . (CH_3).$$

And when zinc-ethyl is heated with iodide of ethyl, a similar action takes place, but attended with formation of free ethyl:—

$$C_2H_5 . Zn + C_2H_5I = ZnI + (C_2H_5) . (C_2H_5).$$

Moreover, the boiling points and vapour-densities of these radicals are related to each other and to those of the compound radicals, methyl-ethyl, butyl-amyl, &c., in a manner which can only be explained by supposing the radicals in the free state to consist of double atoms. This will be seen from the following Table:—

		Sp. gr. at t° C.	Vapour-density.	Boiling-point.
Ethyl-butyl .	$C_2H_5 . C_4H_9$	0·7011	3·053	62° C.
Ethyl-amyl .	$C_2H_5 . C_5H_{11}$	0·7069	3·522	88
Butyl . .	$C_4H_9 . C_4H_9$	0·7057	4·070	106
Butyl-amyl .	$C_4H_9 . C_5H_{11}$	0·7247	4·465	132
Amyl . .	$C_5H_{11} . C_5H_{11}$	0·7413	4·956	158
Butyl-caproyl	$C_4H_9 . C_6H_{13}$	?	4·917	155
Caproyl . .	$C_6H_{13} . C_6H_{13}$	0·7564	5·983	202

The regular gradation of these densities and boiling points plainly shows that the proper places of butyl, amyl, and caproyl in the series, are those which they occupy in the table, and consequently that their atomic weights in the free state are double of those which appertain to them in combination: *e. g.*, amyl in combination = C_5H_{11} = 71; free amyl = $(C_5H_{11})_2$ = 142.

Fourthly: Elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus chlorine acting upon potash forms two compounds, chloride of potassium and hypochlorite of potash:—

$$KKO + ClCl = ClK + ClKO;$$

just as chloride of cyanogen would form chloride of potassium and cyanate of potash. The quantity of chlorine which acts upon an atom of potash, is not 1 at. = 35·5, but 2 at. = 70. Similarly, when metallic sulphides oxidise in the air, both the metal and the sulphur enter into combination with oxygen. Sulphur acting upon potash forms a sulphide and a hyposulphite. Lastly, when zinc-ethyl is exposed to the action of chlorine, iodine, &c., these elements unite separately with the zinc and with the ethyl, thus:—

$$C_2H_5Zn + ClCl = C_2H_5Cl + ZnCl.$$

Double Decomposition regarded as the Type of Chemical Action in general.—Double decomposition is generally understood as an action taking place between four elements or groups of elements; but since it appears that homogeneous atoms may exhibit towards one another the same chemical relations as atoms of different bodies, it follows that the same kind of action may be supposed to take place when less than four bodies are concerned. The extension of this view of chemical action to cases in which three elements or groups of elements come into play, is sufficiently illustrated by the examples just given. But we may proceed still further in the same

direction, and regard as double decompositions those reactions which are commonly viewed as the simple combination or separation of two elements, or as the substitution of one element for another. Thus, when potassium burns in chlorine gas, the reaction may be supposed to take place between two atoms of chlorine and two atoms of potassium:—

$$KK + ClCl = KCl + KCl.$$

Again, the decomposition of cyanide of mercury by heat may be represented thus:—

$$CyHg \,.\, CyHg = CyCy + HgHg.$$

The simple replacement of one element by another may also be regarded as a double decomposition, by supposing the formation of an intermediate compound to take place. Thus, the action of zinc upon hydrochloric acid may be supposed to consist of two stages:—

$$ZnZn + HCl = ZnH + ZnCl,$$

and

$$ZnH + HCl = ZnCl + HH.$$

It is true that the formation of the intermediate compound, the hydride of zinc, cannot be actually demonstrated in this case, because it is decomposed as fast as it is formed; but in other cases the two stages of the action can be distinctly traced. Thus, it is well known that hydrochloric acid does not dissolve copper; but an alloy of zinc and copper, Cu_2Zn, dissolves in it readily, with evolution of hydrogen. Here it may be supposed that the first products are chloride of zinc and hydride of copper, a known compound:—

$$Cu_2Zn + HCl = Cu_2H + ZnCl;$$

and that the hydride is afterwards acted upon by the acid in the manner already explained. Again, when zinc and iodide of ethyl are heated together in a sealed tube, iodide of zinc and zinc-ethyl are obtained, thus:—

$$ZnZn + (\text{Є}_2H_5) \,.\, I = ZnI + Zn(\text{Є}_2H_5);$$

and the zinc-ethyl, when heated with excess of iodide of ethyl, yields iodide of zinc and free ethyl:—

$$Zn\,(C_2H_5) + (C_2H_5).\,I = ZnI + (C_2H_5)\,(C_2H_5).$$

In this manner, all chemical reactions may be reduced to one type, viz., a mutual interchange of atoms between two binary groups.

TYPES AND RADICALS.—RATIONAL FORMULÆ.

The rational formula of a compound is inferred from its modes of formation and decomposition. When cyanide of sodium is mixed with nitrate of silver, an interchange of elements takes place, resulting in the formation of nitrate of soda and cyanide of silver:—

$$CN\,.\,Na + NO_3\,.\,Ag = CN\,.\,Ag + NO_3\,.\,Na.$$

Here the group, or radical NO_3 passes from the silver to the sodium, and in a similar manner it may be transferred to potassium, barium, copper, &c. Hence it may be inferred that the nitrates consist of NO_3 associated with a metal. Similarly, CN may be regarded as the radical of the cyanides; SO_4 of the sulphates, &c. When alcohol, C_2H_6O, is treated with potassium, one-sixth of the hydrogen is evolved, and the compound C_2H_5KO is formed. Again,—alcohol treated with chloride, bromide, and iodide of phosphorus, yields the compounds, C_2H_5Cl, C_2H_5Br, and C_2H_5I; and when the compound C_2H_5KO is treated with C_2H_5I, iodide of potassium and ether are formed:—

$$C_2H_5I + \left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O = KI + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$$

From these and other reactions, alcohol and its derivatives are supposed to contain the radical ethyl, C_2H_5, alcohol being

its hydrated oxide, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$, analogous to hydrate of potash, $\left.\begin{matrix}K\\H\end{matrix}\right\}O$, and ether its anhydrous oxide, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$, analogous to $\left.\begin{matrix}K\\K\end{matrix}\right\}O$.

It must be especially observed, however, that the reason for admitting the existence of ethyl as a radical in the alcohol compounds, is that this supposition affords the readiest explanation of certain reactions. Other reactions may point to a different conclusion. Thus, since alcohol heated to a high temperature with strong sulphuric acid is resolved into olefiant gas and water, it may be regarded as a hydrate of olefiant gas, $C_2H_4 . H_2O$. Again,—certain sulphates, when heated to redness, give off anhydrous sulphuric acid; and sulphate of baryta may be formed by the direct combination of the same anhydrous acid with anhydrous baryta. Such reactions might lead to the conclusion that oxygen-salts are compounds of anhydrous metallic oxides with anhydrous acids, rather than of metals with salt-radicals, which is, in fact, the ordinary view. Similarly, ammoniacal salts are regarded as compounds of NH_3 with hydrated acids, or of NH_4 with acid radicals, according to the reactions specially under consideration.

It appears, then, that the same compound may have several rational formulæ. This of course implies that the formula is an expression, not of the constitution of the body in a state of rest, but of the manner in which the atoms are supposed to arrange themselves when subjected to certain influences. It is no longer the question what the absolute constitution of a substance may be, but of how many forms of constitution the substance fulfils the conditions. For in chemical substances, as in the objects of a branch of natural history, any one individual exhibits more or less distinctly the features of every other.

The greater the number of elementary atoms entering into

the constitution of a compound, the more numerous will be the possible arrangements of those atoms, and the greater, therefore, the number of rational formulæ which may be assigned to the compound. Practically, however, it is found that a small number of rational formulæ—seldom more than two or three—suffices for each compound; and moreover, that the formulæ of all bodies whatever may be reduced to a small number of general types. Of these, Gerhardt adopts four, viz.:—

Water, $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$, from which are derived the oxides, sulphides, selenides, and tellurides.

Hydrochloric acid, HCl, the type of the chlorides, bromides, iodides, fluorides, and cyanides.

Ammonia, $N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$, the type of the nitrides, phosphides, arsenides, &c.

Hydrogen, HH, the type of the elementary bodies, compound radicals, hydrides of metals and radicals, &c.

These typical formulæ all correspond to 2 volumes of vapour.

The formulæ of the several compounds included under each of these types are obtained by replacing one or more of the elementary atoms contained in them by another radical, simple or compound. The derivative compound is called *primary*, *secondary*, or *tertiary*, according to the number of atoms of hydrogen in the type which are thus replaced. For example, the hydrated metallic oxides, which are formed from the type water by the substitution of 1 at. of a metal for 1 at. hydrogen, are primary oxides; *e.g.* hydrate of potash, $\left.\begin{matrix}H\\K\end{matrix}\right\}\Theta$; the anhydrous oxides, in which both atoms of hydrogen are similarly

replaced, as in anhydrous potash, $\left.\begin{matrix}K\\K\end{matrix}\right\}\Theta$, are secondary oxides. The replacement of 1 at. H in ammonia by ethyl, $\rlap{-}C_2H_5$, forms a primary nitride, viz., ethylamine, $N(\rlap{-}C_2H_5)H_2$; similarly, biethylamine, $N(\rlap{-}C_2H_5)_2H$, is a secondary nitride; and triethylamine, $N(C_2H_5)_3$, a tertiary nitride.

Equivalent Values of Radicals.—A radical is *monatomic, biatomic, triatomic*, &c., according as its atom or molecule is equivalent to one, two, three, &c., atoms of hydrogen. Potassium and ethyl are monatomic radicals. *Sulphuryl*, $S\Theta_2$, is a biatomic radical, and by replacing 2 at. H in two molecules of water, $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}\Theta_2$, forms hydrated sulphuric acid, $\left.\begin{matrix}S\Theta_2\\H_2\end{matrix}\right\}\Theta$. *Phosphoryl*, $P\Theta$, is a triatomic radical, and by replacing 3 atoms of hydrogen in three molecules of water, $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}\Theta_3$, forms the ordinary hydrate of phosphoric acid, $PH_3\Theta_4 = \left.\begin{matrix}P\Theta\\H_3\end{matrix}\right\}\Theta_3$.

When a metal forms two classes of salts, its atom has a different equivalent value in each. Thus, in the platinous compounds, Pt (= 98) is monatomic; in the platinic salts, it is biatomic: thus, platinic chloride $= Pt\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$. In the ferrous compounds, Fe (= 28) is monatomic; in the ferric compounds, it is sesquiatomic, Fe_2 being equivalent to H_3, or $Fe_{\frac{2}{3}}$ to H: thus, ferric oxide $= \left.\begin{matrix}Fe_2\\Fe_2\end{matrix}\right\}\Theta_3$. In the mercuric compounds, Hg (=100) is monatomic; in the mercurous compounds, it is semi-atomic; the double atom, Hg_2 (= 200), being the equivalent of 1 atom of hydrogen. In arsenious acid, $As_2\Theta_3$, which is derived from 3 molecules of water, As_2 is equivalent to H_6, and therefore As to H_3; but in arsenic acid, $As_2\Theta_5$, derived from 5 molecules of water, As is equivalent to H_5.*

* If the notion of equivalents be strictly adhered to, independently of the atomic theory, the formulæ of bisalts and sesquisalts may be dispensed with,

Since a compound may have several rational formulæ, or, in other words, may be represented as containing different radicals, it is necessary to determine the relation which exists between the equivalents of such radicals. This relation is determined by the following general law:—*Every equivalent of hydrogen added to a radical diminishes by unity the equivalent value of the entire radical; and every equivalent of hydrogen subtracted from a radical increases by unity the total equivalent value of the entire radical.* Thus, nitric acid may be represented by the three following formula:—

$$\left.\begin{matrix}N\Theta_2\\H\end{matrix}\right\}\Theta, \qquad \left.\begin{matrix}N\Theta\\H\end{matrix}\right\}\Theta_2, \qquad \left.\begin{matrix}N\\H\end{matrix}\right\}\Theta_3.$$

In the first of these formulæ, which represents nitric acid as formed from one molecule of water, $H_2\Theta$, the radical *nitryl*, $N\Theta_2$, is equivalent to 1 atom of hydrogen; in the second, which is formed from 2 molecules of water, $H_4\Theta_2$, the radical *azotyl*, $N\Theta$, formed from nitryl by abstraction of Θ, the equivalent of H_2, takes the place of 3 atoms of hydrogen; and in the third, which is formed from 3 molecules of water, $H_6\Theta_3$, the radical *nitricum*, N, formed from nitryl by abstraction of Θ_2, the equivalent of H_4, takes the place of 5 atoms of hydrogen. Again, uranic oxide may be represented either as $\left.\begin{matrix}U_2\\U_2\end{matrix}\right\}\Theta_3$,

and the different classes of salts of the same metal regarded as containing different radicals: thus the mercurous salts may be regarded as salts of *mercurosum*, Hg = 200; the mercuric salts as containing *mercuricum*, hg = 100: thus—

Mercurous chloride or chloride of mercurosum . .	$HgCl = 200 + 35\cdot5$
Mercuric chloride or chloride of mercuricum . . .	$hgCl = 100 + 35\cdot5$
Ferrous chloride or chloride of ferrosum	$FeCl = 28 + 35\cdot5$
Ferric chloride or chloride of ferricum	$feCl = 18\frac{2}{3} + 35\cdot5$

This mode of representation might be made consistent with the atomic theory, by supposing that the ultimate atom of iron weighs $9\frac{1}{3}$; that a double atom of iron constitutes ferricum = $18\frac{2}{3}$; and a triple atom, ferrosum, = 28: similarly, the atom of mercury weighing 100, a double atom constitutes mercurosum. In organic compounds, such relations between radicals are actually observed: thus, ethylene, C_2H_4, $= 2 \times CH_2$; propylene, C_3H_6, $= 3 \times CH_2$; butylene, $C_4H_8 = 4 \times CH_2$, &c.

or as $\left.\begin{matrix}U_2O\\ U_2O\end{matrix}\right\}O$. The first of these formulæ represents three molecules of water, H_6O_3, and contains the radical $U_2 = H_3$; the second represents one molecule of water, and contains the radical *uranyl*, U_2O, equivalent to H; and accordingly, $U_2 - O$, is equivalent to $H_3 - H_2 = H$. Another example of the general law above stated is afforded by the radicals of the monatomic, biatomic, and triatomic alcohols (p. 531).

Conjugate Radicals.—Any compound radical may be regarded as a compound of two or more simpler radicals. Thus, ethyl, C_2H_5, may be represented as $CH_2 + CH_3$, or as $C_2H_3 + H_2$; acetyl, C_2H_3O, the radical of acetic acid, may be regarded as $CO + CH_3$, or as $C_2H_3 + O$, &c. Radicals viewed in this manner are said to be *conjugated.* A radical may be conjugated either by addition, as in the preceding examples, or by substitution of another radical for one or more atoms of hydrogen; *e. g.*, from benzoyl, C_7H_5O, is formed nitro-benzoyl, $C_7H_4(NO_2)O$, by substitution of a molecule of nitryl, NO_2, for 1 at. H. Similarly, from acetyl, C_2H_3O, are formed monochloracetyl, $C_2(H_2Cl)O$, and terchloracetyl, C_2Cl_3O.

An important class of conjugate radicals consists of those which are formed of certain metals—arsenic, antimony, tin, bismuth, &c.—associated with the alcohol-radicals. For example: cacodyl, or arsen-bimethyl, $As(CH_3)_2$; stibethyl, $Sb(C_2H_5)_3$; arsenethylium, $As(C_2H_5)_4$; stannethyl, $Sn.C_2H_5$. The same radicals may be regarded as conjugated by substitution: *e. g.*, arsenethyl, $As(C_2H_5)_3$, as formed from ammonia, NH_3, the 3 at. H being replaced by ethyl, and the nitrogen by arsenic. In like manner, arsenethylium, $As(C_2H_5)_4$, may be derived from ammonium, NH_4.

The equivalent in hydrogen of a conjugate radical may be determined by the two following rules, deduced from the general law given at page 525:—

1. *The equivalent in hydrogen of a radical conjugated by addition is equal to the difference of the equivalents of the con-*

stituent radicals. Thus, acetyl $(\not{C}_2H_3)\Theta$, which is equivalent to H, is composed of acetosyl, $\not{C}_2H_3$, eq. to H, and Θ eq. to H_2; arsenethyl As $(\not{C}_2H_5)_3$, which is equivalent to H_2, is composed of As (arsenicum), eq. to H_5*, and $(\not{C}_2H_5)_3$, eq. to H_3; cacodyl, As $(\not{C}H_3)_2$, which is equivalent to H, is composed of As (arsenosum), eq. to H_3, and $(\not{C}H_3)_2$ eq. to H_2.

2. *The equivalent in hydrogen of a radical conjugated by substitution is equal to the difference between the sum of the equivalents of the constituent radicals and the equivalent of the hydrogen replaced.* For example,—acetyl $\not{C}_2H_3\Theta$, which is equivalent to H, may be regarded as $\not{C}_2H_5 + \Theta$ (eq. to $H + H_2$) *minus* H_2.

CLASSIFICATION OF CHEMICAL COMPOUNDS.

Bodies may be classified in two ways. 1. According to their origin, as when the acids, salts, oxides, &c., of copper are made to form one group; those of chromium another, those of ethyl a third, &c. 2. According to their chemical functions, independently of origin; the acids forming one group, the bases a second, the alcohols a third, the ethers a fourth, &c. The former mode of classification is best adapted to the detailed description of compounds; the latter for giving a general view of their mutual relations.

The following table exhibits Gerhardt's system of classification by types, or according to chemical functions:—

* Oxide of arsenethyl is $As(\not{C}_2H_5)_3\Theta$ or $As_2(C_2H_5)_6\Theta_2$; now as $(\not{C}_2H_5)_2$ is equivalent to Θ; this last formula may be derived from that of arsenic acid, $As_2\Theta_5$ or $As_2\Theta_3.\Theta_2$ by the substitution of $(\not{C}_2H_5)_6$ for Θ_3; hence As has in oxide of arsenethyl the same equivalent value that it has in arsenic acid; that is to say, it is equivalent to H_5. On the other hand, oxide of cacodyl is $As_2(\not{C}H_3)_4\Theta$; which has the same equivalent value as $As_2.\Theta_2\Theta$, or $As_2\Theta_3$, which is the formula of arsenious acid. Hence the radical As in cacodyl has the same value as in arsenious acid, viz., equivalent to H_3.

	WATER TYPE, $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$.		HYDROCHLORIC- HCl.
	OXIDES.	SULPHIDES (Selenides, Tellurides).	CHLORIDES (Bromides, Iodides, Fluorides).
Derivatives with Positive Radicals.	**Bases proper.**	**Basic Sulphides.**	**Basic Chlorides.**
	1. *Primary* or *hydrated bases* (hydrate of potash $\left.\begin{matrix}H\\K\end{matrix}\right\}\Theta$, hydrate of arsenethylium).	1. *Primary* or *hydrosulphates* (hydrosulphate of potassium).	*Metallic chlorides* (chloride of potassium).
	2. *Secondary* or *anhydrous bases* (oxide of potassium).	2. *Secondary* or *metallic sulphides* (sulphide of potassium).	. . . .
	Alcohols or Hydrocarburetted Bases.	**Alcoholic Sulphides.**	**Alcoholic Chlorides.**
	1. *Primary* or *alcohols proper* (vinic alcohol, hydrate of phenyl, glycol, glycerine).	1. *Primary* or *mercaptans* (hydrosulphate of ethyl).	*Hydrochloric ethers* (chloride of ethyl).
	2. *Secondary alcohols* or *ethers* (oxide of ethyl).	2. *Secondary* or *hydrosulphuric ethers* (sulphide of ethyl).	. . . .
	Aldehydes.	**Aldehydic Sulphides.**	**Aldehydic Chlorides.**
	1. *Primary* (acetic aldehyde, bitter almond oil).	1. *Primary* (sulphobenzol).	Chloride of aldehydene.
	2. *Secondary.*	2. *Secondary.*	. . . .
Derivatives with Negative Radicals.	**Acids.**	**Acid Sulphides.**	**Acid Chlorides.**
	1. *Primary* or *hydrated acids* (sulphuric, acetic, cyanic acids).	1. *Primary* (hydrosulphocyanic acid).	Chloride of acetyl, oxychloride of phosphorus, chloride of cyanogen, free chlorine.
	2. *Secondary* or *anhydrous acids.*	2. *Secondary* (sulphide of benzoyl).	. . . .
Intermediate Derivatives.	**Oxygen-salts.**	**Sulphur-salts.**	
	Sulphates, nitrates, cyanates.	Sulphocyanides, sulphantimoniates.	. . . .
	Compound Ethers.	**Compound Sulphur-ethers.**	
	Sulphate, cyanate, oxalate of ethyl, glycerides, stearin, &c.	Thiacetate of ethyl, sulphocyanide of ethyl.	. . . .
	Compound Aldehydes.	**Compound Sulphur-aldehydes.**	

ACID-TYPE,	AMMONIA TYPE, $N\left\{\begin{matrix}H\\H.\\H\end{matrix}\right.$	HYDROGEN TYPE, HH.
CYANIDES.	NITRIDES (Phosphides).	METALS (Metalloïds).
Basic Cyanides.	**Basic Nitrides.**	**Basic Metals.**
Metallic cyanides (cyanide of potassium, ferrocyanide of potassium).	1. *Primary* (amide of potassium).	1. *Primary* or *metallic hydrides* (hydride of copper).
. . . .	2. *Secondary.* 3. *Tertiary* (nitride of potassium).	2. *Secondary* or *metals proper* (potassium, stibethyl, tetrethylium).
Alcoholic Cyanides.	**Alcoholic Nitrides.**	**Alcoholic Metals.**
Hydrocyanic ethers or *nitriles* (acetonitrile, hydrocyanic acid).	1. *Primary* (ethylamine).	1. *Primary* or *alcoholic hydrides* (marsh-gas, benzin).
. . . .	2. *Secondary* (biethylamine). 3. *Tertiary* (triethylamine).	2. *Secondary*: the so-called *alcohol-radicals* (ethyl, amyl, phenyl).
Aldehydic Cyanides.	**Aldehydic Nitrides.**	**Aldehydic Metals.**
. . . .	1. *Primary.*	1. *Primary* or *aldehydic hydrides* (olefiant gas).
. . . .	2. *Secondary.* 3. *Tertiary.*	2. *Secondary.*
Acid Cyanides.	**Acid Nitrides.**	**Acid Metals.**
Cyanide of benzoyl, free cyanogen.	1. *Primary* (benzamide, cyanamide, succinamide).	1. *Primary* or *acid hydrides* (hydride of benzoyl, hydrochloric acid, hydrocyanic acid).
. . . .	2. *Secondary* (succinimide, benzoyl-phenylamide). 3. *Tertiary* (bibenzoyl-salicylamide, boramide, free nitrogen).	2. *Secondary* or *metalloids* (benzoyl, chlorine, cyanogen).
. . . .	**Amidogen-salts.** Benzamidate of mercury.	Here might be placed many compounds already included in the preceding classes: *e.g.*, the cyanides of ethyl, &c., containing the radical of cyanic acid and an alcohol-radical.
. . . .	**Alcalamides.** Oxanilide, ethylacetamide.	

WATER-TYPE.

Positive Oxides.—*A. Bases proper, or Metallic Oxides.*— These compounds are formed by the substitution of a metallic radical, simple or compound, for the hydrogen, in one, two, or three molecules of water:—

α. Monatomic.—Hydrate of potash, $\left.\begin{matrix}K\\H\end{matrix}\right\}\Theta$; anhydrous potash or oxide of potassium, $\left.\begin{matrix}K\\K\end{matrix}\right\}\Theta$;—cupric hydrate, $\left.\begin{matrix}Cu\\H\end{matrix}\right\}\Theta$;— cupric oxide, $\left.\begin{matrix}Cu\\Cu\end{matrix}\right\}\Theta$;—hydrate of ammonium, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}\Theta$;— hydrate of tetramercurammonium, $\left.\begin{matrix}NHg_4\\H\end{matrix}\right\}\Theta$;— hydrate of tetrethylium, $\left.\begin{matrix}N(\mathrm{C}_2H_5)_4\\H\end{matrix}\right\}\Theta$;—oxide of cacodyl, $\left.\begin{matrix}As(\mathrm{C}H_3)_2\\As(CH_3)_2\end{matrix}\right\}\Theta$;— oxide of arsenethylium, $\left.\begin{matrix}As(\mathrm{C}_2H_5)_4\\As(\mathrm{C}_2H_5)_4\end{matrix}\right\}\Theta$.

β. Biatomic.— Platinic hydrate, $\left.\begin{matrix}Pt\\H_2\end{matrix}\right\}\Theta_2$; platinic oxide, $\left.\begin{matrix}Pt\\Pt\end{matrix}\right\}\Theta_2$; oxide of stibethyl, $\left.\begin{matrix}Sb(\mathrm{C}_2H_5)_3\\Sb(C_2H_5)_3\end{matrix}\right\}\Theta_2$.*

γ. Triatomic. — Hydrate of alumina, $\left.\begin{matrix}Al_2\\H_3\end{matrix}\right\}\Theta_3$; anhydrous alumina, $\left.\begin{matrix}Al_2\\Al_2\end{matrix}\right\}\Theta_3$; antimonic hydrate, $\left.\begin{matrix}Sb\\H_3\end{matrix}\right\}\Theta_3$; antimonic oxide, $\left.\begin{matrix}Sb\\Sb\end{matrix}\right\}\Theta_3$; teroxide of bismuth, $\left.\begin{matrix}Bi\\Bi\end{matrix}\right\}\Theta_3$

Certain triatomic bases may be represented as monatomic, by supposing a portion of the oxygen to be associated with the positive radical; thus, sesquioxide of uranium $U_4\Theta_3$ may be represented as protoxide of uranyl, $\left.\begin{matrix}U_2\Theta\\U_2\Theta\end{matrix}\right\}\Theta$; and teroxide of antimony, $Sb_2\Theta_3$, as protoxide of antimonyl, $\left.\begin{matrix}Sb\Theta\\Sb\Theta\end{matrix}\right\}\Theta$. Non-

* The radical stibethyl is biatomic, like arsenethyl (p. 527).

basic bioxides, or peroxides, may be represented in a similar manner; *e.g.*, peroxide of hydrogen, $= \left.\begin{matrix}HO\\H\end{matrix}\right\}O$.

B. Alcohols.—These bodies, all of which belong to organic chemistry, are also monatomic, biatomic, or triatomic. The *primary monatomic alcohols*, or *alcohols proper*, are derived from water by the replacement of 1 atom of hydrogen by a hydrocarbon of the form C_nH_{2n+1}; C_nH_{2n-1}; or C_nH_{2n-7}.

a. Alcohols containing radicals of the form C_nH_{2n+1}. The number of these at present known is ten, viz.:—

Methylic alcohol, wood-spirit, or hydrate of methyl (protyl) . .	$CH_4O = \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O$.
Ethylic alcohol, spirit of wine, or hydrate of ethyl (deutyl) . .	$C_2H_6O = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$.
Propylic alcohol, or hydrate of trityl	$C_3H_8O = \left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}O$.
Butylic alcohol, or hydrate of tetryl	$C_4H_{10}O = \left.\begin{matrix}C_4H_9\\H\end{matrix}\right\}O$.
Amylic alcohol, or hydrate of amyl (pentyl)	$C_5H_{12}O = \left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}O$.
Caproic alcohol, or hydrate of hexyl	$C_6H_{14}O = \left.\begin{matrix}C_6H_{13}\\H\end{matrix}\right\}O$.
Caprylic alcohol, or hydrate of octyl.	$C_8H_{18}O = \left.\begin{matrix}C_8H_{17}\\H\end{matrix}\right\}O$.
Cetylic alcohol, or hydrate of cetyl.	$C_{16}H_{34}O = \left.\begin{matrix}C_{16}H_{33}\\H\end{matrix}\right\}O$.
Cerylic alcohol, or hydrate of ceryl	$C_{27}H_{56}O = \left.\begin{matrix}C_{27}H_{55}\\H\end{matrix}\right\}O$.
Melissic alcohol, or hydrate of melissyl	$C_{30}H_{62}O = \left.\begin{matrix}C_{30}H_{61}\\H\end{matrix}\right\}O$.

The first of these liquids is found among the products of the destructive distillation of wood; the second, third, fourth, and fifth, are formed by the fermentation of saccharine sub-

stances; caprylic alcohol is obtained by saponifying castor-oil with hydrate of potash and distilling the product with excess of the alkali at a high temperature; cetylic alcohol is obtained from spermaceti; cerylic alcohol from Chinese wax, and melissic alcohol from bees-wax.

Compounds, whose formulæ differ from one another by $n \cdot CH_2$, are said to be *homologous: e. g.*, the alcohols, the fatty acids (p. 538), the compound ethers (p. 545), &c.

β. Alcohols containing radicals of the form C_nH_{2n-1}: —

Acrylic or allylic alcohol, $C_3H_6\Theta = \left.\begin{matrix}C_3H_5\\H\end{matrix}\right\}\Theta$. This is the only term of the series at present known.

γ. Alcohols containing the radicals, C_nH_{2n-7}: — Of this series, there are two isomeric groups, distinguished by their behaviour with oxidising agents, the bodies of the one group being thereby converted into aldehydes, the others not. To the first group belong:—

Benzoic alcohol . .	$C_7H_8\Theta$	=	$\left.\begin{matrix}C_7H_7\\H\end{matrix}\right\}\Theta$.
Cuminic alcohol . .	$C_{10}H_{14}\Theta$	=	$\left.\begin{matrix}C_{10}H_{13}\\H\end{matrix}\right\}\Theta$.

To the second:—

Phenylic alcohol, carbazotic acid, or hydrate of phenyl . .	$C_6H_6\Theta$	=	$\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}\Theta$.
Cresylic alcohol . .	$C_7H_8\Theta$	=	$\left.\begin{matrix}C_7H_7\\H\end{matrix}\right\}\Theta$.

All these alcohols contain 1 atom of hydrogen replaceable by a metal; thus: common alcohol, treated with potassium, gives off one sixth of its hydrogen, and yields ethylate of potassium, $\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}\Theta$. It is not found possible to replace another atom of hydrogen in a similar manner.

Biatomic Alcohols, or Glycols.—The general formula of these compounds is $\left.\begin{matrix}C_nH_{2n}\\H_2\end{matrix}\right\}\Theta_2$. Three of them have been obtained,

viz., ethylic glycol, $\left.\begin{matrix}C_2H_4\\ H_2\end{matrix}\right\}O_2$; propylic glycol, $\left.\begin{matrix}C_3H_6\\ H_2\end{matrix}\right\}O_2$; and amylic glycol, $\left.\begin{matrix}C_5H_{10}\\ H_2\end{matrix}\right\}O_2$. The 2 at. hydrogen in each of these formulæ, may be replaced by other radicals positive or negative; so that the glycols are bibasic and biacid. By mixing iodide of ethylene, $C_2H_4 . I_2$ with 2 atoms of acetate of silver, and distilling the product, a distillate of acetate of glycol is obtained, while iodide of silver remains behind: —

$$C_2H_4I_2 + 2\underbrace{\left(\left.\begin{matrix}C_2H_3O\\ Ag\end{matrix}\right\}O\right)}_{\text{Acetate of silver.}} = 2\ AgI + \underbrace{\left.\begin{matrix}C_2H_4\\ (C_2H_3O)_2\end{matrix}\right\}O_2}_{\text{Acetate of glycol.}};$$

and acetate of glycol distilled with hydrate of potash yields glycol and acetate of potash:—

$$\left.\begin{matrix}C_2H_4\\ (C_2H_3O)_2\end{matrix}\right\}O_2 + 2\left(\left.\begin{matrix}K\\ H\end{matrix}\right\}O\right) = \left.\begin{matrix}C_2H_4\\ H_2\end{matrix}\right\}O_2 + 2\left(\left.\begin{matrix}C_2H_3O\\ K\end{matrix}\right\}O\right)$$

The propylic and amylic glycols are obtained in a similar manner with bromide of propylene and bromide of amylene.

Triatomic Alcohols, or Glycerines.—The general formula of these compounds is $\left.\begin{matrix}C_nH_{2n-1}\\ H_3\end{matrix}\right\}O_3$. The three atoms of hydrogen which they contain may be wholly or partly replaced by radicals positive or negative. One term of the series has been long known, viz.: ordinary glycerine, $C_3H_8O_3 = \left.\begin{matrix}C_3H_5\\ H_3\end{matrix}\right\}O_3$. The neutral fats, olein, stearin, palmitin, &c., consist of glycerin, in which the 3 atoms of free hydrogen are replaced by acid radicals; *e. g.*, stearin, $C_{57}H_{110}O_6 = \left.\begin{matrix}C_3H_5\\ (C_{18}H_{35}O)_3\end{matrix}\right\}O_3$. A great number of similar compounds have been formed artificially by heating glycerine with acids. Conversely, when neutral fats, stearin for example, are heated

with hydrate of potash, or other metallic oxides, the acid radical passes to the metal, forming a salt, and glycerine is formed, *e.g.*,

$$\left.\begin{matrix}Ȼ_3H_5\\(Ȼ_{18}H_{35}Ɵ)_3\end{matrix}\right\}Ɵ_3 + 3\left(\begin{matrix}K\\H\end{matrix}Ɵ\right) = 3\left(\begin{matrix}Ȼ_{18}H_{35}Ɵ\\K\end{matrix}\right)Ɵ_3 + \left.\begin{matrix}Ȼ_3H_5\\H_3\end{matrix}\right\}Ɵ_3.$$

This is the process of saponification. Glycerine may also be formed synthetically, viz. by heating the terbromide of allyl, $Ȼ_3H_5Br_3$ with acetate of silver. Teracetate of glycerine (triacetin) is thus formed; and this, when heated with hydrate of baryta, yields glycerine. The other glycerines have not yet been obtained in the free state; but the acetate of ethyl-glycerine, $\left.\begin{matrix}Ȼ_2\dot{H}_3\\(Ȼ_2H_3Ɵ)_3\end{matrix}\right\}Ɵ_3$, is obtained at the same time as glycol, by the action of iodide of ethylene on acetate of silver.

The *secondary alcohols*, or *Ethers*, bear the same relation to the primary alcohols that anhydrous metallic oxides bear to the hydrates; *e.g.*, amylic alcohol, $\left.\begin{matrix}Ȼ_5H_{11}\\H\end{matrix}\right\}Ɵ$; amylic ether, $\left.\begin{matrix}Ȼ_5H_{11}\\Ȼ_5H_{11}\end{matrix}\right\}Ɵ$.

There are likewise ethers containing two different radicals; *e. g.*, methyl-amylic ether, $\left.\begin{matrix}ȻH_3\\Ȼ_5H_{11}\end{matrix}\right\}Ɵ$. Ethers may be formed by the action of the iodides of methyl, ethyl, &c., on alcohols in which 1 atom of hydrogen is replaced by potassium; thus, common alcohol treated with potassium gives off hydrogen, and yields $Ȼ_2H_5KƟ$; and this compound treated with iodide of amyl, yields ethyl-amylic ether:—

$$\left.\begin{matrix}Ȼ_2H_5\\K\end{matrix}\right\}Ɵ + Ȼ_5H_{11}I = KI + \left.\begin{matrix}Ȼ_2H_5\\Ȼ_5H_{11}\end{matrix}\right\}Ɵ.$$

The same potassium-alcohol treated with iodide of ethyl, yields common ether:—

$$\left.\begin{matrix}Ȼ_2H_5\\K\end{matrix}\right\}Ɵ + Ȼ_2H_5 . I = KI + \left.\begin{matrix}Ȼ_2H_5\\Ȼ_2H_5\end{matrix}\right\}Ɵ.$$

Ethers are also formed by the action of strong sulphuric acid on the alcohols, as will be more fully explained hereafter.

C.—*Aldehydes.*—These compounds differ from the alcohols, in containing 2 atoms of hydrogen less. Thus, to an alcohol, $\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}O$, there corresponds an aldehyde, $\left.\begin{matrix}C_nH_{2n-1}\\H\end{matrix}\right\}O$. They are obtained by the action of oxidising agents on the alcohols. Thus, common alcohol treated with bichromate of potash and sulphuric acid, yields ethylic or acetic aldehyde, $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O$.

There are likewise aldehydes corresponding to the other series of alcohols. Thus, to the alcohols containing the radicals, C_nH_{2n-7}, there correspond aldehydes containing radicals of the form C_nH_{2n-9}. Oil of bitter almonds, $C_7H_6O = \left.\begin{matrix}C_7H_5\\H\end{matrix}\right\}O$, belongs to the series.

The aldehydes are especially distinguished by forming crystalline compounds with the alkaline bisulphites; *e. g.*, sulphite of acetosyl and sodium, $C_2H_3NaO, SO_2 = \left.\begin{matrix}SO\\C_2H_3.Na\end{matrix}\right\}O_2$.

One atom of hydrogen in the radical of an aldehyde may be replaced by an alcohol-radical; the compounds thus produced are called *ketones*. Thus, acetone, C_3H_6O, the ketone of the acetic series, is $\left.\begin{matrix}C_2H_2(CH_3)\\H\end{matrix}\right\}O$.

Acids, or Negative Oxides.—These, like the positive oxides, are divided into primary or hydrated, and secondary or anhydrous. Thus, hydrated nitric acid, $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$; anhydrous nitric acid, $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$.

Acids are also monatomic, like nitric acid just noticed, and acetic acid, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$; biatomic, like sulphuric acid, $\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$;

or triatomic, as phosphoric acid, $\left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3$; citric acid, $\left.\begin{matrix}C_6H_5O_4\\H_3\end{matrix}\right\}O_3$.

A monatomic hydrated acid, having only one atom of replaceable hydrogen, is necessarily monobasic; a biatomic acid, having two atoms of replaceable hydrogen, is generally (but not necessarily) bibasic; a triatomic acid, generally tribasic. The determination of the basicity of an acid is a matter of some difficulty. In many cases, the formation or non-formation of acid and double salts may serve as a distinction. Thus, tartaric acid, which is a bibasic acid, $\left.\begin{matrix}C_4H_4O_4\\H_2\end{matrix}\right\}O_2$, forms a neutral tartrate of potash, $\left.\begin{matrix}C_4H_4O_4\\K_2\end{matrix}\right\}O_2$, and an acid tartrate, $\left.\begin{matrix}C_4H_4O_4\\KH\end{matrix}\right\}O_2$; so, likewise, sulphuric acid forms SK_2O_4, and $SKHO_4$; whereas nitric acid, having but one atom of hydrogen, forms but one potash-salt, viz. NKO_3. But acetic acid, generally regarded as monobasic, $C_2H_4O_2 = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$, also forms, not only a neutral potash-salt, $C_2H_3KO_2$, but likewise, an acid potash-salt, usually represented by the formula $C_2H_3KO_2 . C_2H_4O_2$; but if the formula of acetic acid be doubled, making it $C_4H_8O_4$, the neutral potash-salt will be $C_4H_6K_2O_4$, and the acid salt, $C_4H_6(KH)O_4$. Acetic acid will thus be represented as a bibasic acid; and in fact, this quantity, $C_4H_8O_4$ ($=120$), is the equivalent of SH_2O_4 ($=98$), that is to say, it saturates the same quantity of potash. Why, then, is acetic acid universally regarded as monobasic? On this point, we shall quote the observations of Gerhardt:—

"The basicity of acids is a question, not of equivalents, but of molecules. . . . If we examine, *under the same volume*, the composition of the vapour of certain volatile bodies, corresponding to the acids, and compare together the similar terms, such as the chlorides of the acid radicals, or the neutral compound ethers, we observe perfectly regular differences, which are

always related to the chemical properties of the corresponding bodies: thus,—

$$2 \text{ vol. of} \left\{\begin{matrix}\text{Chloride of acetyl} & \text{. contain} & Cl\,.\,C_2H_3O. \\ \text{Chloride of sulphuryl} & ,, & Cl_2\,.\,SO_2.\end{matrix}\right.$$

$$2 \text{ vol. of} \left\{\begin{matrix}\text{Acetate of methyl} & \text{. contain} & \left.\begin{matrix}C_2H_3O\\ CH_3\end{matrix}\right\}O. \\ \text{Sulphate of methyl .} & ,, & \left.\begin{matrix}SO_2\\ (CH_3)_2\end{matrix}\right\}O_2.\end{matrix}\right.$$

In the same volume, therefore, chloride of acetyl contains the radical chlorine once, while chloride of sulphuryl contains it twice: In the same volume, again, sulphate of methyl contains twice the quantity of methyl that is contained in the acetate. With these differences of composition of the chlorides and neutral ethers, are connected other properties, such as the following:—Acetic acid forms but one compound ether (p. 545), whereas sulphuric acid forms two, a neutral and an acid ether; acetic acid forms but one amide (p. 557); sulphuric acid forms several, &c. In short, on inquiring what are the smallest quantities of the radicals, acetyl and sulphuryl, that are concerned in chemical metamorphoses, we find that they are C_2H_3O, equivalent to H, and SO_2 equivalent to H_2; hence, we are led to represent the molecule of acetic acid as monatomic, and that of sulphuric acid as biatomic."

The principal monobasic inorganic acids are nitric, $\left.\begin{matrix}NO_2\\ H\end{matrix}\right\}O$, hypochlorous, $\left.\begin{matrix}Cl\\ H\end{matrix}\right\}O$, chloric, $\left.\begin{matrix}ClO_2\\ H\end{matrix}\right\}O$, and metaphosphoric, $\left.\begin{matrix}PO_2\\ H\end{matrix}\right\}O$.

Of monobasic organic acids, the most important are the so-called fatty acids, whose general formula is—

$$C_nH_{2n}O_2 = \left.\begin{matrix}C_nH_{2n-1}O\\ H\end{matrix}\right\}O.$$

They correspond to the alcohols $C_nH_{2n+1}O$, and those which contain the same number of carbon atoms as the known alcohols may be obtained from the latter by the action of

oxidising agents, such as chromic acid. The number of these acids at present known to exist is sixteen, viz.:—

Formic acid	CH_2O_2	Œnanthylic acid	$C_7H_{14}O_2$	Palmitic acid	$C_{16}H_{32}O_2$
Acetic „	$C_2H_4O_2$	Caprylic „	$C_8H_{16}O_2$	Stearic „	$C_{18}H_{36}O_2$
Propionic „	$C_3H_6O_2$	Pelargonic „	$C_9H_{18}O_2$	Cerotic „	$C_{27}H_{54}O_2$
Butyric „	$C_4H_8O_2$	Rutic or capric „	$C_{10}H_{20}O_2$	Melissic „	$C_{30}H_{60}O_2$
Valerianic „	$C_5H_{10}O_2$	Lauric „	$C_{12}H_{24}O_2$		
Caproic „	$C_6H_{12}O_2$	Myristic „	$C_{14}H_{28}O_2$		

These acids occur in the vegetable and animal organism; they are formed by the saponification of fats, and by the action of oxidising agents on fatty and waxy matters, and on albumin, fibrin, casein, &c. The first ten acids of the series are liquid at ordinary temperatures; the next four are solid fats; the last two are waxy. Cerotic acid is obtained from Chinese wax; melissic acid from bees-wax.

A second series of monobasic organic acids consists of acids whose radical is of the form $C_nH_{2n-3}O$; *e. g.*, oleic acid, $C_{18}H_{34}O_2 = \left.\begin{matrix}C_{18}H_{33}\\ H\end{matrix}\right\}O$, obtained by the saponification of various fixed oils. A third series consists of acids whose radical has the form $C_nH_{2n-9}O$. These are called the *aromatic acids;* only three of them are known, viz. benzoic acid, $\left.\begin{matrix}C_7H_5O\\ H\end{matrix}\right\}O$; toluic acid, $\left.\begin{matrix}C_8H_7O\\ H\end{matrix}\right\}O$, and cuminic acid, $\left.\begin{matrix}C_{10}H_{11}O\\ H\end{matrix}\right\}O$.

There are a few monatomic organic acids not included in either of these groups, among which, must be particularly mentioned cyanic acid, $\left.\begin{matrix}CN\\ H\end{matrix}\right\}O$. The cyanates are formed from the cyanides by oxidation; thus, cyanide of potassium fused with oxide of lead, or bioxide of manganese, yields cyanate of potash, $CNKO$.

Bibasic acids.—These acids, as already observed, generally form two salts, a neutral and an acid salt, and are peculiarly inclined to form double salts; *e. g.* potassio-cupric sulphate, $\left.\begin{matrix}SO_2\\ KCu\end{matrix}\right\}O_2$; tartrate of potash and soda, $\left.\begin{matrix}C_4H_4O_4\\ KNa\end{matrix}\right\}O_2$.

With the alcohols they form two compound ethers, a neutral and an acid ether; *e. g.*, neutral oxalate of ethyl, $\left.\begin{matrix}C_2O_2\\(C_2H_5)_2\end{matrix}\right\}O_2$; acid oxalate of ethyl, or oxalovinic acid, $\left.\begin{matrix}C_2O_2\\H\,(C_2H_5)\end{matrix}\right\}O_2$.

Within the same vapour volume, the neutral ethers of the bibasic acids contain twice as much of the alcohol-radical as the neutral ethers of the monobasic acids (p. 545). Thus, 2 vols. oxalate of ethyl $= \left.\begin{matrix}C_2O_2\\(C_2H_5)_2\end{matrix}\right\}O$; 2 vols. benzoate of ethyl $= \left.\begin{matrix}C_7H_5O\\C_2H_5\end{matrix}\right\}O$.

The chlorides of bibasic acids (obtained by the action of pentachloride of phosphorus on the acids) *contain, within a given vapour volume, twice as much chlorine as the chlorides of the monobasic acids* (p. 549).

The principal bibasic inorganic acids are carbonic, $\left.\begin{matrix}CO\\H_2\end{matrix}\right\}O_2$; sulphurous, $\left.\begin{matrix}SO\\H_2\end{matrix}\right\}O_2$; sulphuric, $\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2$; and chromic acid, $\left.\begin{matrix}Cr_2O_2\\H_2\end{matrix}\right\}O_2$. Pyro-phosphoric acid, $P_2H_4O_7$, may be regarded as bibasic acid, containing the radical $P_2H_2O_5$; viz., $\left.\begin{matrix}P_2H_2O_5\\H_2\end{matrix}\right\}O_7$; or as a compound of metaphosphoric and ordinary phosphoric acid.

The greater number of the bibasic organic acids may be arranged in three groups, viz.:—

α.—Acids whose general formula is $\left.\begin{matrix}C_nH_{2n-4}O_2\\H_2\end{matrix}\right\}O_2$. Eight of these are known, viz.:—Oxalic acid, $\left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2$; succinic acid ($C_4$); pyro-tartaric ($C_5$); adipic ($C_6$); pimelic ($C_7$); suberic ($C_8$); anchoic ($C_9$); and sebacic acid ($C_{10}$). They are formed by the action of oxidising agents on fatty matters, and are related to the monobasic fatty acids $C_nH_{2n}O_4$ by the relation —

$$C_nH_{2n-2}O_4 = CO_2 + C_{n-1}H_{2n-2}O_2$$

$$e.\,g.,\quad \underbrace{C_4H_6O_4}_{\text{Succinic acid.}} = CO_2 + \underbrace{C_3H_6O_2}_{\text{Propionic acid.}}$$

β.—General formula: $\left.\begin{matrix}(C_nH_{2n-1}O_2)_2\\ H_2\end{matrix}\right\} O_2$. For example, lactic acid $= C_6H_{12}O_6 = \left.\begin{matrix}(C_3H_5O_2)_2\\ H_2\end{matrix}\right\} O_2$.

γ.—General formula: $\left.\begin{matrix}C_nH_{2n-10}O_2\\ H_2\end{matrix}\right\} O_2$. Two acids of this group are known, viz., phthalic acid, $C_8H_6O_4$, obtained by the action of nitric acid on bichloride of naphthalin, and insolinic acid, $C_9H_8O_4$, by the action of chromic acid on cuminic acid. They are related to the aromatic acids in the same manner as the acids α to the fatty acids. Thus:—

$$\underbrace{C_9H_8O_4}_{\text{Insolinic acid.}} = CO_2 + \underbrace{C_8H_8O_2}_{\text{Toluic acid.}}$$

Of bibasic acids not included in the preceding groups, the most important are malic acid, $C_4H_6O_5 = \left.\begin{matrix}C_4H_4O_3\\ H_2\end{matrix}\right\} O_2$; and tartaric acid, $C_4H_6O_6 = \left.\begin{matrix}C_4H_4O_4\\ H_2\end{matrix}\right\} O_2$.

Tribasic acids.—These acids, containing three atoms of replaceable hydrogen, form three kinds of salts, viz., one neutral, and two acid salts. Thus, from tribasic phosphoric acid, $PH_3O_4 = \left.\begin{matrix}PO\\ H_3\end{matrix}\right\} O_3$ are formed PH_2KO_4, PHK_2O_4, and PK_3O_4.

With alcohols they form three compound ethers. Phosphoric acid and common alcohol yield ethylophosphoric acid, $PH_2(C_2H_5)O_4$; bi-ethylophosphoric acid, $PH(C_2H_5)_2O_4$; phosphoric ether, $P(C_2H_5)_3O_4$.

The neutral ethers of tribasic acids contain, within a given vapour volume, three times as much of the alcohol radical as the ethers of the monobasic acids. Thus, 2 vols. citric ether contain $\left.\begin{matrix}C_6H_5O_4\\ (C_2H_5)_3\end{matrix}\right\} O_3$; and 2 vols. acetic ether contain $\left.\begin{matrix}C_2H_3O\\ C_2H_5\end{matrix}\right\} O$.

The chlorides of the tribasic acid radicals contain, within a given volume, three times as much chlorine as the chlorides of the monobasic acid radicals. Thus, 2 vols. chloride of phosphoryl

(oxychloride of phosphorus) contain $P\Theta . Cl_3$; and 2 vols. chloride of benzoyl contain $C_7H_5\Theta . Cl$.

The tribasic mineral acids are,—boracic acid, $BH_3\Theta_3$; phosphorous acid, $PH_3\Theta_3$; phosphoric acid, $PH_3\Theta_4$; and arsenic acid, $AsH_3\Theta_5$.

Five tribasic organic acids are known, viz.:—

$$\text{Cyanuric acid } C_6H_3N_3\Theta_3 = \left.\begin{matrix}Cy_3\\H_3\end{matrix}\right\}\Theta_3.$$

$$\text{Citric acid . } C_6H_8\Theta_7 = \left.\begin{matrix}C_6H_5\Theta_4\\H_3\end{matrix}\right\}\Theta_3.$$

$$\text{Aconitic acid . } C_6H_6\Theta_6 = \left.\begin{matrix}C_6H_3\Theta_3\\H_3\end{matrix}\right\}\Theta_3.$$

$$\text{Meconic acid . } C_7H_4\Theta_7 = \left.\begin{matrix}C_7H\Theta_4\\H_3\end{matrix}\right\}\Theta_3.$$

$$\text{Chelidonic acid } C_7H_4\Theta_6 = \left.\begin{matrix}C_7H\Theta_3\\H_3\end{matrix}\right\}\Theta_3.$$

Cyanuric acid may be regarded as a triple molecule of cyanic acid. It is formed by the destructive distillation of uric acid, by the action of chlorine gas on urea, and by the action of water on fixed chloride of cyanogen, Cy_3Cl_3. Aconitic acid is obtained by the destructive distillation of citric acid. Meconic acid is contained in opium, and chelidonic acid in the *chelidonium majus*.

Conjugated acids.—This name is given to acids containing a conjugated radical. Thus, there are *chloro-*, *bromo-*, and *iodo-conjugated* acids, containing chlorine, bromine, or iodine in place of hydrogen in the radical; *e. g.*, chloracetic acid, $\left.\begin{matrix}C_2(Cl_2H)\Theta\\H\end{matrix}\right\}\Theta$; terchloracetic acid, $\left.\begin{matrix}C_2Cl_3\Theta\\H\end{matrix}\right\}\Theta$: *nitro-conjugated* acids, containing $N\Theta_2$; *e. g.*, nitro-benzoic acid, $\left.\begin{matrix}C_7H_4(N\Theta_2)\Theta\\H\end{matrix}\right\}\Theta$: *sulpho-conjugated* acids, containing $S\Theta_2$; *e g.*, sulpho-benzoic acid, $\left.\begin{matrix}C_7H_4(S\Theta_2)\Theta\\H_2\end{matrix}\right\}\Theta_2$, &c.

These acids are formed by the action of sulphuric acid, nitric acid, chlorine, &c., on the primitive acids:—

$$\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O + \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}C_7H_4(NO_2)O\\H\end{matrix}\right\}O.$$

$$\left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O + \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}C_7H_4(SO_2)O\\H_2\end{matrix}\right\}O_2.$$

α.—Amidogen acids.—These are derived from hydrate of ammonium, $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}O$, by the substitution of an acid radical for two or more atoms of the hydrogen in ammonium. Thus:—

Sulphamic acid . .	SH_3NO_3	=	$\left.\begin{matrix}NH_2SO_2\\H\end{matrix}\right\}O.$
Phosphamic acid .	PH_2NO_2	=	$\left.\begin{matrix}NH(PO)\\H\end{matrix}\right\}O.$
Osmiamic acid . .	Os_2HNO_3	=	$\left.\begin{matrix}N(Os_2O_2)\\H\end{matrix}\right\}O.$
Oxamic acid . .	$C_2H_3NO_3$	=	$\left.\begin{matrix}NH_2(C_2O_2)\\H\end{matrix}\right\}O.$

These acids are formed by the action of ammonia on the anhydrides, or by the action of heat on the acid ammonia-salts of bibasic acids, an atom of water being thus eliminated:—

$$\underbrace{\left.\begin{matrix}C_2O_2\\H.(NH_4)\end{matrix}\right\}O_2}_{\text{Acid oxalate of ammonia.}} - H_2O = \underbrace{\left.\begin{matrix}NH_2(C_2O_2)\\H\end{matrix}\right\}O.}_{\text{Oxamic acid.}}$$

Anhydrous Acids, or Anhydrides.—These compounds are formed by the substitution of an acid radical for the whole of the hydrogen in one or two molecules of water, thus:—citric anhydride $N_2O_5 = \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$; sulphuric anhydride $SO_3 = SO_2.O$; phosphoric anhydride $P_2O_5 = \left.\begin{matrix}PO\\PO\end{matrix}\right\}O_3$.

Anhydrous nitric acid is obtained by the action of chlorine on dry nitrate of silver. The anhydrides of bibasic acids may be formed by the abstraction of water from the hydrated acids, either by heat or by the action of anhydrous phosphoric acid; *e.g.*:—

$$\underbrace{\left.\begin{matrix}C_4H_4O_2\\H_2\end{matrix}\right\}O_2}_{\text{Succinic acid.}} - H_2O = \underbrace{C_4H_4O_2 \,.\, O}_{\text{Succinic anhydride.}}$$

The bibasic acids may, indeed, be supposed to contain water. Thus, succinic acid $= C_4H_4O_2 \,.\, O + H_2O$. But the anhydrides of the monobasic acids cannot be obtained in this way; in fact, according to the formulæ of the unitary system, they do not contain water, and even supposing H_2O to be abstracted from them, the remainder will not be the formula of the anhydrides: thus, the formula of acetic acid being $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$, the abstraction of H_2O would leave C_2H_2O; whereas, the formula of anhydrous acetic acid is $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O = 2 \times C_2H_3O_{\frac{3}{2}}$. This is a fact which the ordinary formulæ do not explain. If the formula of hydrated acetic acid be $C_4H_4O_4 = C_4H_3O_3 \,.\, HO$, it is by no means evident why the HO should not be separated from it, and leave the anhydrous acid.

The anhydrides of organic monobasic acids are obtained by the action of the chlorides of their radicals on the alkaline salts of the acids; thus:—

$$\underbrace{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O}_{\text{Acetate of potash.}} + \underbrace{C_2H_3O \,.\, Cl}_{\text{Chloride of acetyl.}} = KCl + \underbrace{\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O}_{\text{Acetic anhydride.}}$$

There are some organic anhydrides containing two different radicals; thus, by the action of chloride of benzoyl on acetate of potash, aceto-benzoic anhydride is formed:—

$$\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O + C_7H_5O \,.\, Cl = KCl + \left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O.$$

These compounds are resolved by heat into the simple anhydrides, thus:—

$$\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\} + \left.\begin{matrix}C_7H_5O\\C_7H_5O\end{matrix}\right\}O.$$

Oxygen-salts, or Intermediate Oxides.—Salts are formed by the substitution of a metal or other positive radical for the basic hydrogen of an acid, and may therefore be regarded as water, the hydrogen of which is replaced partly by a basic, partly by an acid radical. If all the basic hydrogen of the acid is thus replaced, the salt is *neutral* or *normal;* if only part of the hydrogen is thus replaced, the salt is *acid;* and such salts may be regarded as compounds of neutral salts with the free acid, thus:—

$$\underbrace{2\left(\left.\begin{matrix}SO_2\\NaH\end{matrix}\right\}O_2\right)}_{\text{Bisulphate of soda.}} = \underbrace{\left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2}_{\text{Sulphuric acid.}} + \underbrace{\left.\begin{matrix}SO_2\\Na_2\end{matrix}\right\}O_2}_{\text{Neutral sulphate of soda.}}$$

$$\underbrace{\left.\begin{matrix}(C_2H_3O)_2\\KH\end{matrix}\right\}O_2}_{\text{Biacetate of potash.}} = \underbrace{\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O}_{\text{Acetic acid.}} + \underbrace{\left.\begin{matrix}C_2H_3O\\K\end{matrix}\right\}O.}_{\text{Neutral acetate of potash.}}$$

Basic salts may be regarded as compounds of a neutral salt and an oxide, or as double or triple molecules of water, in which the hydrogen is replaced by a positive radical in a larger proportion than is required to form a neutral salt; thus:—

$$\underbrace{\left.\begin{matrix}C_2H_3O\\Pb_3\end{matrix}\right\}O_2}_{\text{Subacetate of lead.}} = \underbrace{\left.\begin{matrix}Pb\\Pb\end{matrix}\right\}O}_{\text{Oxide of lead.}} + \underbrace{\left.\begin{matrix}C_2H_3O\\Pb\end{matrix}\right\}O.}_{\text{Neutral acetate of lead.}}$$

$$\underbrace{\left.\begin{matrix}SO_2\\Cu_4\end{matrix}\right\}O_3}_{\text{Subsulphate of copper.}} = \underbrace{\left.\begin{matrix}Cu\\Cu\end{matrix}\right\}O}_{\text{Oxide of copper.}} + \underbrace{\left.\begin{matrix}Cu_2\\SO_2\end{matrix}\right\}O_2}_{\text{Neutral sulphate of copper.}}$$

In the neutral salts of sesquioxides, as in the oxides themselves, 3 at. hydrogen of the type water are replaced by 2 at. of the metal; thus —

$$\underbrace{\left.\begin{matrix}(N\Theta_2)_3\\ Fe_2\end{matrix}\right\}\Theta_3}_{\text{Ferric nitrate.}}; \qquad \underbrace{\left.\begin{matrix}(S\Theta_2)_3\\ Fe_4\end{matrix}\right\}\Theta_6}_{\text{Ferric sulphate.}}.$$

Compound ethers. When the basic hydrogen of an acid is replaced by an alcohol-radical, the product is a compound ether; these compounds may also be regarded as alcohols in which one atom of hydrogen is replaced by an acid radical. As already observed, monobasic acids form but one compound ether; bibasic acids form two, a neutral and an acid ether; and tribasic acids, one neutral and two acid ethers. The acid ethers are true acids, and form salts. Thus, from sulphuric acid are formed —

$$\text{Neutral sulphate of ethyl} = \left.\begin{matrix}S\Theta_2\\ (C_2H_5)_2\end{matrix}\right\}\Theta_2, \text{ and}$$

$$\begin{matrix}\text{Acid sulphate of ethyl, or}\\ \text{sulphovinic acid}\end{matrix} = \left.\begin{matrix}S\Theta_2\\ H\\ C_2H_5\end{matrix}\right\}\Theta_2.$$

The remaining atom of hydrogen in the latter may be replaced by K, Na, &c.

From citric acid are formed —

$$\text{Neutral citrate of methyl} \quad . \quad . \quad . \quad \left.\begin{matrix}C_6H_5\Theta_4\\ (CH_3)_3\end{matrix}\right\}\Theta_3$$

$$\text{Citrobimethylic acid (monobasic)} \quad . \quad \left.\begin{matrix}C_6H_5\Theta_4\\ (CH_3)_2\\ H\end{matrix}\right\}\Theta_3$$

$$\text{Citromonomethylic acid (bibasic)} \quad . \quad \left.\begin{matrix}C_6H_5\Theta_4\\ CH_3\\ H_2\end{matrix}\right\}\Theta_3$$

The *glycerides* or *neutral fats* (p. 533) also belong to the compound ethers, being derived from a triatomic alcohol or glycerine by the substitution of an acid radical for the replaceable hydrogen; *e.g.*, triacetin = $\left.\begin{matrix}C_3H_5\\ (C_2H_3\Theta)_3\end{matrix}\right\}\Theta_3$.

SULPHIDES, SELENIDES, TELLURIDES.

The formulæ of these bodies are precisely similar to those of the oxides, being derived from hydrosulphuric acid, $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, &c. just as the oxides are derived from water. These series, however, especially the selenides and tellurides, are much less complete than that of the oxides.

The analogy between the metallic sulphides and oxides has been sufficiently pointed out in the preceding part of this work. The alkali-metals, potassium, sodium, &c., form hydrated sulphides, or hydro-sulphates, such as $\left.\begin{matrix}K\\H\end{matrix}\right\}S$, $\left.\begin{matrix}Ba\\H\end{matrix}\right\}S$, &c.; and anhydrous sulphides, $\left.\begin{matrix}K\\K\end{matrix}\right\}S$, &c. Most of the other metals form only anhydrous sulphides.

The *alcoholic sulphides*, primary and secondary, bear the same relation to hydrosulphuric acid that the alcohols and ethers bear to water. The primary alcoholic sulphides, $\left.\begin{matrix}C_nH_{2n+1}\\H\end{matrix}\right\}S$, generally called *mercaptans*, are fetid oils, or crystalline solids, which are obtained by the action of the alkaline hydrosulphates on the chlorides of the alcohol radicals:—

$$\underbrace{C_2H_5Cl}_{\text{Chloride of ethyl.}} + \left.\begin{matrix}K\\H\end{matrix}\right\}S = KCl + \underbrace{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S}_{\text{Ethylic mercaptan.}};$$

or by the action of the same alkaline hydrosulphates on the sulphovinates or homologous salts:—

$$\left.\begin{matrix}SO_2\\K,C_2H_5\end{matrix}\right\}O_2 + \left.\begin{matrix}K\\H\end{matrix}\right\}S = \left.\begin{matrix}SO_2\\K_2\end{matrix}\right\}O_2 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S.$$

The basic hydrogen in the mercaptans may be replaced by metals, forming compounds called *mercaptides; e. g.*, $\left.\begin{matrix}C_2H_5\\Hg\end{matrix}\right\}S$.

The secondary alcoholic sulphides or hydrosulphuric ethers are obtained by the action of the anhydrous alkaline sulphides on the chlorides of the alcohol-radicals:—

$$2C_2H_5Cl + \left.\begin{matrix}K\\K\end{matrix}\right\}S = 2KCl + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S.$$

Sulphur-acids.—The mineral sulphur-acids are but little known in the hydrated state. The anhydrous sulphur-acids are analogous to the oxygen-acids. Thus, sulpharsenious acid, $\left.\begin{matrix}As\\As\end{matrix}\right\}S_3$, sulpharsenic acid, $\left.\begin{matrix}As\\As\end{matrix}\right\}S_5$, the arsenic being triatomic in the former, and pentatomic in the latter.

But few organic sulphur-acids have been obtained. Hydrosulphocyanic acid, $CNHS = \left.\begin{matrix}Cy\\H\end{matrix}\right\}S$, is analogous to cyanic acid, $\left.\begin{matrix}Cy\\H\end{matrix}\right\}O$. Its potassium-salt is obtained by heating sulphur with ferrocyanide of potassium (I. 532).

Thiacetic acid $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S$, is obtained by the action of pentasulphide of phosphorus on acetic acid:—

$$5\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O\right) + P_2S_5 = P_2O_5 + 5\left(\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S\right).$$

This reaction is instructive when viewed in relation to that of pentachloride of phosphorus on acetic acid; the latter giving rise to two chlorides, $C_2H_3O.Cl$, and HCl, whereas the action of the sulphide of phosphorus yields not two, but one sulphur compound, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S$. A similar difference is observed in the action of the sulphide and chloride of phosphorus on alcohol, the former producing a single compound, viz. mercaptan, the sulphide of ethyl and hydrogen, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$, the latter producing two separate compounds, viz. C_2H_5Cl, and HCl. This difference of action shows in a striking manner the pro-

priety of representing the oxides and sulphides by a type containing two atoms of hydrogen, and the chlorides, bromides, &c., by a type containing only one atom of hydrogen.

Sulphur-salts. — These compounds are formed from the type $\left.\begin{matrix}H\\H\end{matrix}\right\}S$, by the substitution of a positive and a negative radical for the two atoms of hydrogen: Thus, monobasic sulpharseniate of potassium, $\left.\begin{matrix}As\\K\end{matrix}\right\}S_3$; tribasic sulpharseniate of potassium, $\left.\begin{matrix}AsS\\K_3\end{matrix}\right\}S_3$; these formulæ are evidently analogous to those of the monobasic and tribasic phosphates.

The *compound sulphur-ethers* are sulphur-salts, in which the positive element is an alcohol radical: — For example, sulphocyanide of ethyl, $\left.\begin{matrix}Cy\\C_2H_5\end{matrix}\right\}S$; sulphocyanide of allyl, or oil of mustard, $= \left.\begin{matrix}Cy\\C_3H_5\end{matrix}\right\}S$.

Sulphide of acetyl and ethyl, or thiacetic ether, is obtained by the action of persulphide of phosphorus on acetic acid: —

$$5\left(\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O\right) + P_2S_5 = 5\left(\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}S\right) + P_2O_5.$$

HYDROCHLORIC ACID TYPE.

CHLORIDES. — The *basic metallic chlorides* are, like the oxides, either monatomic or polyatomic; *e. g.* —

$$\underbrace{KCl}_{\text{monatomic.}} \qquad \underbrace{PtCl_2}_{\text{biatomic.}} \qquad \underbrace{Fe_2Cl_3 \,.\, AuCl_3.}_{\text{triatomic.}}$$

The biatomic and triatomic chlorides unite with the monatomic chlorides, forming crystalline compounds, whose composition may be illustrated by the formulæ of —

Chloro-aurate of sodium . . $NaCl \,.\, AuCl_3 = \left.\begin{matrix}Na\\Au\end{matrix}\right\}Cl_4.$

Chloroplatinate of ammonium, $NH_4Cl . PtCl_2 = \left.\begin{matrix}NH_4\\Pt\end{matrix}\right\}Cl_3$.

The chlorides of gold and platinum form similar compounds with the hydrochlorates of the organic bases, which may be represented by analogous formulæ. Thus, chloroplatinate of ethylamine, $\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N . HCl + PtCl_2 = \left.\begin{matrix}NH_3(C_2H_5)\\Pt\end{matrix}\right\}Cl_3$.

The hydrochlorate of any organic alkali may be represented as the chloride of a basic radical containing an additional atom of hydrogen, just as sal-ammoniac may be represented either as $NH_3 . HCl$, or as NH_4Cl. Thus, hydrochlorate of ethylamine, $NH_2(C_2H_5) . HCl = NH_3(C_2H_5) . Cl$.

The *chlorides of the alcohol-radicals*, or *hydrochloric ethers*, are obtained either by the action of hydrochloric acid, or one of the chlorides of phosphorus, on the alcohols:—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + HCl = \left.\begin{matrix}H\\H\end{matrix}\right\}O + C_2H_5 . Cl.$$

$$\left.\begin{matrix}\\ \\ \end{matrix}\right\}O \Big) + PCl_3 = \underbrace{\left.\begin{matrix}P\\H_3\end{matrix}\right\}O_3}_{\text{Phosphorous acid.}} + 3\,(\underbrace{C_2H_5 . Cl}_{\text{Chloride of ethyl.}}).$$

...lorides are more volatile than the corresponding ...

...cid, or *negative chlorides*, are also monatomic, biatomic, ...tomic, according to the acids from which they are ...ed.

...he monatomic chlorides, derived from one atom of hydro...oric acid, contain, in two vapour-volumes, one atom of chlorine, ...pable of forming a metallic chloride with mineral alkalies; e.g., chloride of cyanogen, $CNCl = Cy . Cl$; chloride of acetyl, $= C_2H_3O . Cl$. They are obtained by the action of one of the chlorides of phosphorus on the acids, thus:—

$$\left.\begin{matrix}C_2H_3\Theta \\ H\end{matrix}\right\}\Theta + \underbrace{PCl_2 \,.\, Cl_3}_{\text{Perchloride of phosphorus.}} = \underbrace{\frac{C_2H_3\Theta \,.\, Cl}{HCl}}_{\text{Chloride of acetyl + hydrochloric acid.}} + \underbrace{P\Theta \,.\, Cl_3}_{\text{Oxychloride of phosphorus.}}$$

$$3\left(\left.\begin{matrix}C_2H_3\Theta \\ H\end{matrix}\right\}\Theta\right) + PCl_3 = \left.\begin{matrix}P \\ H_3\end{matrix}\right\}\Theta_3 + 3\,(C_2H_3\Theta . Cl).$$

Or, by the action of oxychloride of phosphorus on an alkaline salt of the same acid:—

$$\left(\left.\begin{matrix}C_2H_3\Theta \\ K\end{matrix}\right\}\Theta\right) + P\Theta . Cl_3 = \left.\begin{matrix}P\Theta \\ K_3\end{matrix}\right\}\Theta_3 + 3\,(C_2H_3\Theta . Cl).$$

The biatomic chlorides, derived from two molecules of hydrochloric acid, contain, within two vapour-volumes, two atoms of chlorine, capable of forming a metallic chloride with alkalies:—

Chloride of carbonyl, oxychloride of carbon, or phosgene	$= C\Theta \,.\, Cl_2$
Chloride of sulphuryl	$= S\Theta_2 \,.\, Cl_2$
Chloride of succinyl	$= C_4H_4\Theta_4 \,.\, Cl_2$
Chloride of chromyl, or chlorochromic acid	$= Cr_2\Theta_2 \,.\, Cl_2$

These chlorides may be obtained by the action of pentachloride of phosphorus upon the corresponding anhydrous acids.

The action of pentachloride of phosphorus on a bibasic acid is supposed by Gerhardt to consist of two stages,—the first being the formation of an anhydrous acid, the second the conversion of that compound into a chloride. For example:—

$$\left.\begin{matrix}C_4H_4\Theta_2 . \Theta \\ H_2 . \Theta\end{matrix}\right\} + PCl_2 . Cl_3 = C_4H_4\Theta_2 . \Theta + 2HCl + P\Theta Cl_3;$$

$$\text{and } C_4H_4\Theta_2 . \Theta + PCl_2 . Cl_3 = C_4H_4\Theta_2 . Cl_2 + P\Theta Cl_3;$$

whereas, in the case of a monobasic acid, the action consists of one stage only. This difference is connected by Gerhardt

with the fact, that a bibasic acid may be supposed to contain water, whereas a monobasic acid cannot (p. 543). According to Williamson, on the contrary, the two stages of the reaction, in the case of a bibasic acid, are precisely similar to one another, and to the single reaction which takes place with monobasic acids. Thus, with sulphuric acid—

$$\left.\begin{matrix}\mathrm{S\Theta_2}\\ \mathrm{H_2}\end{matrix}\right\}\Theta_2 + \mathrm{PCl_2 \,.\, Cl_3} = \left.\begin{matrix}\mathrm{S\Theta_2}\\ \mathrm{HCl}\end{matrix}\right\}\Theta + \mathrm{HCl} + \mathrm{P\Theta Cl_3},$$

$$\text{and}\quad \left.\begin{matrix}\mathrm{S\Theta_2}\\ \mathrm{HCl}\end{matrix}\right\}\Theta + \mathrm{PCl_2 \,.\, Cl_3} = \mathrm{S\Theta_2 \,.\, Cl_2} + \mathrm{HCl} + \mathrm{P\Theta Cl_3}.$$

The difference in the two views of the reaction is this:—that the former supposes the first stage of the action to consist in the formation of an anhydrous acid; the second supposes an intermediate compound,—a chloro-hydrate of the acid, to be produced. The formation of this chloro-hydrate has been shown by Professor Williamson to take place with sulphuric acid. If, however, one of the two molecules of hydrochloric acid in Gerhardt's first equation be supposed to remain associated with the anhydrous acid, the two views will nearly coincide. In every case, indeed, the reaction consists essentially in the interchange of Θ and Cl_2.

The triatomic chlorides, or terchlorides, contain, within two vapour volumes, three atoms of chlorine capable of forming a metallic chloride when acted upon by the mineral alkalies.

The following acid chlorides are triatomic:—

Terchloride of phosphorus	$\mathrm{P \,.\, Cl_3}$
Chloride of phosphoryl (oxychloride of phosphorus	$\mathrm{P\Theta \,.\, Cl_3}$
Chloride of sulphophosphoryl (sulphochloride of phosphorus)	$\mathrm{P\cancel{S} \,.\, Cl_3}$
Chloride of chlorophosphoryl (pentachloride of phosphorus)	$\mathrm{PCl_2 \,.\, Cl_3}$

Chloride of boron . . . . $B . Cl_3$

Chloride of cyanuryl (solid chloride of cyanogen) $Cy_3 . Cl_3$

The BROMIDES, IODIDES, and FLUORIDES, are exactly analogous to the chlorides. There are very few organic fluorides known.

The CYANIDES are also analogous to the chlorides.

The *metallic cyanides* have a great tendency to unite and form double cyanides, which may be regarded as derivatives of two or more atoms of hydrochloric acid. Thus, the *ferro-cyanides* may be represented by the formula $\left.\begin{matrix}Fe\\M_2\end{matrix}\right\}Cy_3$, and the *ferricyanides*, by $\left.\begin{matrix}M_3\\Fe_2\end{matrix}\right\}Cy_6$; the Fe_2 in the latter formula being equivalent to H_3.

The *cyanides of the alcohol-radicals* are obtained by distilling a sulphovinate or homologous salt with cyanide of potassium: thus,—

$$\left.\begin{matrix}S\Theta_2\\K . C_2H_5\end{matrix}\right\}\Theta_2 + KCy = \left.\begin{matrix}S\Theta_2\\K_2\end{matrix}\right\}\Theta_2 + C_2H_5 . Cy;$$

or by the action of anhydrous phosphoric acid on the ammoniacal salts of the fatty acids, the action of the phosphoric acid consisting in the abstraction of water: thus,—

$$\underbrace{\left.\begin{matrix}C_2H_3\Theta\\NH_4\end{matrix}\right\}\Theta}_{\text{Acetate of ammonia.}} - 2H_2\Theta = \underbrace{CN . CH_3}_{\text{Cyanide of methyl.}};$$

or, generally,

$$\left.\begin{matrix}C_nH_{2n-1}\Theta\\NH_4\end{matrix}\right\}\Theta - 2H_2\Theta = CN . C_{n-1}H_{2n-1}.$$

The ammonia-salt of each acid in the series yields when thus treated, the cyanide, not of the corresponding alcohol-radical, but of the next lowest; thus: the propionate yields cyanide of ethyl; the acetate, cyanide of methyl; and the formiate, cyanide of hydrogen, or hydrocyanic acid.

When these cyanides are heated with caustic alkalies, the opposite change takes place; that is to say, an alkaline salt of the acid corresponding to the next highest alcohol is formed, and ammonia is evolved: thus,—

$$\underbrace{\text{CNH}}_{\substack{\text{Cyanide}\\\text{of hy-}\\\text{drogen.}}} + \left.\begin{matrix}\text{H}\\\text{K}\end{matrix}\right\}\text{O} + \text{H}_2\text{O} = \underbrace{\left.\begin{matrix}\text{CHO}\\\text{K}\end{matrix}\right\}\text{O}}_{\substack{\text{Formiate of}\\\text{potash.}}} + \text{NH}_3;$$

$$\underbrace{\text{CN}.\text{CH}_3}_{\substack{\text{Cyanide of}\\\text{methyl.}}} + \left.\begin{matrix}\text{H}\\\text{K}\end{matrix}\right\}\text{O} + \text{H}_2\text{O} = \underbrace{\left.\begin{matrix}\text{C}_2\text{H}_3\text{O}\\\text{K}\end{matrix}\right\}\text{O}}_{\substack{\text{Acetate of}\\\text{potash.}}} + \text{NH}_3;$$

$$\text{CN}.\text{C}_n\text{H}_{2n+1} + \left.\begin{matrix}\text{H}\\\text{K}\end{matrix}\right\}\text{O} + \text{H}_2\text{O} = \left.\begin{matrix}\text{C}_{n+1}\text{H}_{2n+1}\text{O}\\\text{K}\end{matrix}\right\}\text{O} + \text{NH}_3.$$

These alcoholic cyanides may also be regarded as nitriles: thus,—

$$\underbrace{\text{CNH}}_{\substack{\text{Cyanide}\\\text{of hy-}\\\text{drogen.}}} = \underbrace{\text{N}.\text{CH}}_{\substack{\text{Formo-}\\\text{nitrile.}}}; \qquad \underbrace{\text{CN}.\text{CH}_3}_{\substack{\text{Cyanide of}\\\text{methyl.}}} = \underbrace{\text{N}.\text{C}_2\text{H}_3}_{\substack{\text{Aceto-}\\\text{nitrile}}};$$

generally: $\text{CN}.\text{C}_n\text{H}_{2n+1} = \text{N}.\text{C}_{n+1}\text{H}_{2n+1}$.

AMMONIA TYPE.

NITRIDES.—*a. Positive.*—These compounds are chiefly organic, constituting in fact the organic bases or alkaloids. A few mineral nitrides have, however, been obtained by the action of ammonia on the metals or their oxides; *e.g.*, amide of potassium, $N(H_2K)$; nitride of potassium, NK_3; nitride of mercury NHg_3.

The primary nitrides of the alcohol-radicals, such as methylamine, $CH_5N = N(CH_3 . H_2)$, amylamine $C_5H_{13}N =$

$N(\text{Ɵ}_5H_{11}.H_2)$, are obtained:—1. By the action of the bromides or iodides of the alcohol-radicals on ammonia:—

$$NH_3 + \underbrace{\text{Ɵ}_2H_5I}_{\text{Iodide of ethyl.}} = HI + \underbrace{N\left\{\begin{matrix}\text{Ɵ}_2H_5\\ H.\\ H\end{matrix}\right.}_{\text{Ethylamine.}}$$

2. By the action of potash on the cyanates or cyanurates of the same radicals:—

$$\underbrace{N\left\{\begin{matrix}\text{ƟΘ}\\ \text{Ɵ}_2H_5\end{matrix}\right.}_{\text{Cyanate of ethyl.}} + \underbrace{\left.\begin{matrix}H_2\\ K_2\end{matrix}\right\}\Theta_2}_{\text{Hydrate of potash.}} = \underbrace{\left.\begin{matrix}\text{ƟΘ}\\ K_2\end{matrix}\right\}\Theta_2}_{\text{Carbonate of potash.}} + \underbrace{N\left\{\begin{matrix}\text{Ɵ}_2\\ H.\\ H\end{matrix}\right.}_{\text{Ethylamine.}}$$

3. By the action of reducing agents, such as hydrosulphuric acid, or acetate of iron, on certain nitro-conjugated hydrocarbons; thus:—

$$\underbrace{\text{Ɵ}_6H_5(N\Theta_2)}_{\text{Nitrobenzol.}} + 3H_2S = \underbrace{N\left\{\begin{matrix}\text{Ɵ}_6H_5\\ H\\ H\end{matrix}\right.}_{\text{Aniline or phenylamine.}} + 2H_2\Theta + 3S.$$

They are also frequently produced in the destructive distillation of nitrogenised organic substances, and are consequently found in coal-tar, bone-oil, &c.

These bodies are all volatile liquids, having more or less of an ammoniacal odour. The bases of the same series—for instance, those formed from the alcohol-radicals Ɵ_nH_{2n+1}— are less volatile and more oily, as they contain more carbon. They all combine with acids in the same manner as ammonia, and form crystallisable double salts with bichloride of platinum. Nitrous acid converts them into alcohols or nitrous ethers, with elimination of nitrogen:—

$$\underbrace{\left.\begin{matrix}\text{Ɵ}_2H_5\\ H\\ H\end{matrix}\right\}N}_{\text{Ethylamine.}} + \underbrace{\left.\begin{matrix}N\\ N\end{matrix}\right\}\Theta_3}_{\text{Nitrous acid.}} = NN + \underbrace{\left.\begin{matrix}\text{Ɵ}_2H_5\\ N\end{matrix}\right\}\Theta_2}_{\text{Nitrite of ethyl.}} + H_2\Theta;$$

$$2\underbrace{\left(\left.\begin{matrix}C_6H_5\\H\\H\end{matrix}\right\}N\right)}_{\text{Aniline.}} + \left.\begin{matrix}N\\N\end{matrix}\right\}O_3 = 2\,NN + 2\underbrace{\left(\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}O\right)}_{\text{2 mol. hydrate of phenyl.}} + H_2O.$$

Secondary alcoholic nitrides.—The constitution of these bodies may be understood from the following examples:—

Biethylamine, $C_4H_{11}N$ . . $= \left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N.$

Metethylamine, C_3H_9N . . $= \left.\begin{matrix}C_2H_5\\CH_3\\H\end{matrix}\right\}N.$

Ethaniline, or ethyphenylamine, $C_8H_{11}N = \left.\begin{matrix}C_2H_5\\C_6H_5\\H\end{matrix}\right\}N.$

They are obtained by the action of the bromides or iodides of the alcohol-radicals on the primary nitrides:—

$$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N + C_2H_3Br = \left.\begin{matrix}C_2H_3\\C_2H_5\\H\end{matrix}\right\}N + HBr.$$

Tertiary alcoholic nitrides, or *nitrile bases*:—

Triethylamine, $C_6H_{15}N = \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N.$

Biethamylamine $C_9H_{21}N = \left.\begin{matrix}C_2H_5\\C_2H_5\\C_5H_{11}\end{matrix}\right\}N.$

Methamylaniline $C_{12}H_{19}N = \left.\begin{matrix}CH_3\\C_5H_{11}\\C_6H_5\end{matrix}\right\}N.$

These compounds are formed by the action of the iodides and bromides of the alcohol-radicals on the secondary alcoholic nitrides; also by the distillation of the ammonium-bases, thus:—

$$\underbrace{\left.\begin{matrix}N(\mathrm{C}_2H_5)_4\\ H\end{matrix}\right\}\mathrm{O}}_{\text{Hydrate of tetrethylium.}} = \underbrace{(\mathrm{C}_2H_5)_3N}_{\text{Triethylamine.}} + \underbrace{\mathrm{C}_2H_4}_{\text{Ethylene.}} + H_2\mathrm{O}.$$

Triethylamine is likewise obtained by the action of ethylate of potassium on cyanate of ethyl:—

$$\underbrace{N\left\{\begin{matrix}\mathrm{CO}\\ \mathrm{C}_2H_5\end{matrix}\right.}_{\text{Cyanate of ethyl.}} + \underbrace{\left.\begin{matrix}(\mathrm{C}_2H_5)_2\\ K_2\end{matrix}\right\}\mathrm{O}_2}_{\text{2 at. ethylate of potassium.}} = \underbrace{\left.\begin{matrix}\mathrm{CO}\\ K_2\end{matrix}\right\}\mathrm{O}_2}_{\text{Carbonate of potash.}} + \underbrace{N(\mathrm{C}_2H_5)_3}_{\text{Triethylamine.}}.$$

This action is analogous to that of hydrate of potash or cyanate of ethyl (p. 554). The other tertiary alcoholic nitrides might doubtless be obtained in a similar manner.

There are also nitrides containing conjugated alcohol-radicals; *e.g.*:—

Bichlorethylamine $\mathrm{C}_2H_5Cl_2N = \left.\begin{matrix}\mathrm{C}_2H_3Cl_2\\ H\\ H\end{matrix}\right\}N.$

Chloraniline . $\mathrm{C}_6H_6ClN = \left.\begin{matrix}\mathrm{C}_6H_4Cl\\ H\\ H\end{matrix}\right\}N.$

Nitraniline . . . $\mathrm{C}_6H_6(NO_2)N = \left.\begin{matrix}\mathrm{C}_6H_4(N\mathrm{O}_2)\\ H\\ H\end{matrix}\right\}N.$

Nitrides of aldehyde-radicals.—These bodies are but little known.

Acetosylamine, $N(H_2 . \mathrm{C}_2H_3)$, is obtained by the action of ammonia on chloride of ethylene (chloride of acetosyl and hydrogen):—

$$\underbrace{\left.\begin{matrix}\mathrm{C}_2H_3\\ H\end{matrix}\right\}Cl_2}_{\text{Chloride of acetosyl and hydrogen.}} + 2\,NH_3 = \underbrace{\left.\begin{matrix}\mathrm{C}_2H_3\\ H\\ H\end{matrix}\right\}N.HCl}_{\text{Hydrochlorate of acetosylamine.}} + NH_4Cl.$$

The natural vegeto-alkalies, morphine, strychnine, &c., are most probably of similar nature to these artificial alkalies, but they have not yet been reduced to regular series.

b. Negative or *acid nitrides.* — These are the compounds generally called *amides.*

Primary amides.—In these compounds, one-third of the hydrogen in 1, 2, or 3 molecules of ammonia is replaced by an acid radical.

α. Monatomic:—

Acetamide, or nitride of acetyl and hydrogen . . . . $\left.\right\} C_2H_5NO = N\left\{\begin{matrix} C_2H_3O \\ H \\ H \end{matrix}\right.$.

Butyramide, or nitride of butyryl and hydrogen . . . . $\left.\right\} C_4H_9NO = N\left\{\begin{matrix} C_4H_7O \\ H \\ H \end{matrix}\right.$.

Benzamide, or nitride of benzoyl and hydrogen . . . . $\left.\right\} C_7H_7NO = N\left\{\begin{matrix} C_7H_5O \\ H \\ H \end{matrix}\right.$.

These amides differ from the corresponding ammoniacal salts by the elements of one atom of water:—

$$\underbrace{\left.\begin{matrix} C_2H_3O \\ NH_4 \end{matrix}\right\} O}_{\text{Acetate of ammonia.}} - H_2O = \underbrace{N\left\{\begin{matrix} C_2H_3O \\ H_2 \end{matrix}\right.}_{\text{Acetamide.}}.$$

They are produced by the action of ammonia on the anhydrous acids:—

$$\underbrace{\left.\begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix}\right\} O}_{\text{Benzoic anhydride.}} + NH_3 = \underbrace{\left.\begin{matrix} C_7H_5O \\ H \end{matrix}\right\} O}_{\text{Benzoic acid.}} + \underbrace{N\left\{\begin{matrix} C_7H_5O \\ H_2 \end{matrix}\right.}_{\text{Benzamide.}};$$

by the action of ammonia on the acid chlorides:—

$$C_7H_5O.Cl + NH_3 = HCl + N\left\{\begin{matrix} C_7H_5O \\ H_2 \end{matrix}\right.;$$

and by the action of ammonia on the compound ethers:—

$$\underbrace{\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O}_{\text{Acetate of ethyl.}} + NH_3 = \underbrace{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O}_{\text{Alcohol.}} + \underbrace{N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.}_{\text{Acetamide.}}.$$

These amides are neutral crystalline bodies, which, when boiled with aqueous acids or alkalies, take up water, and are converted into ammonia-salts. When treated with anhydrous phosphoric acid, they give up the elements of 1 at. water, and are converted into cyanides of the alcohol radicals:—

$$\underbrace{N\left\{\begin{matrix}C_2H_3O\\H_2\end{matrix}\right.}_{\text{Acetamide.}} - H_2O = \underbrace{CN\,.\,CH_3}_{\text{Cyanide of methyl.}}.$$

β. Biatomic. *Primary biamides* or *diamides*:—

Oxamide, or nitride of oxalyl and hydrogen . . . . $C_2H_4N_2O_2 = N_2\left\{\begin{matrix}C_2O_2\\H_2\\H_2\end{matrix}\right.$

Succinamide, or nitride of succinyl and hydrogen . . . . $C_4H_8N_2O_2 = N_2\left\{\begin{matrix}C_4H_4O_2\\H_2\\H_2\end{matrix}\right.$

Urea and carbamide, or nitride of carbonyl and hydrogen . . . $CH_4N_2O = N_2\left\{\begin{matrix}CO\\H_2\\H_2\end{matrix}\right.$

Tartramide, or nitride of tartryl and hydrogen . . . . $C_4H_8N_2O_4 = N_2\left\{\begin{matrix}C_4H_4O_4\\H_2\\H_2\end{matrix}\right.$

They are produced by the action of heat on the neutral ammonia-salts of bibasic acids:—

$$\underbrace{\left.\begin{matrix}C_2O_2\\(NH_4)_2\end{matrix}\right\}O_2}_{\text{Oxalate of ammonia.}} - 2H_2O = \underbrace{N_2\left\{\begin{matrix}C_2O_2\\H_2\\H_2\end{matrix}\right.}_{\text{Oxamide.}};$$

by the combination of ammonia with secondary amides:—

$$\underbrace{N\left\{\begin{matrix}CO\\H\end{matrix}\right.}_{\text{Cyanic acid or carbonimide.}} + NH_3 = \underbrace{N_2\left\{\begin{matrix}CO\\H_2\\H_2\end{matrix}\right.}_{\text{Urea.}};$$

and by the action of ammonia on compound ethers or acid chlorides:—

$$\underbrace{\begin{matrix}C_2O_2\\(C_2H_5)_2\end{matrix}\Big\}O_2}_{\text{Oxalate of ethyl.}} + 2NH_3 = \underbrace{\begin{matrix}H_2\\(C_2H_5)_2\end{matrix}\Big\}O_2}_{\text{2 at. alcohol.}} + \underbrace{N_2\Big\{\begin{matrix}C_2O_2\\H_4\end{matrix}}_{\text{Oxamide.}}$$

$$\underbrace{C_4H_4O_2 . Cl_2}_{\text{Chloride of succinyl.}} + 2NH_3 = 2HCl + \underbrace{N_2\Big\{\begin{matrix}C_4H_4O_2\\H_4\end{matrix}}_{\text{Succinamide.}}$$

γ.—Triatomic. *Primary triamides*:—

Triphosphamide, or nitride of phosphoryl and hydrogen . . $\Big\}$ $N_3\Big\{\begin{matrix}PO\\H_6\end{matrix}$

Citramide, or nitride of citryl and hydrogen . . . . . $\Big\}$ $C_6H_{11}N_3O_4 = N_3\Big\{\begin{matrix}C_6H_5O_4\\H_6\end{matrix}$

Melamine and melam, or nitride of cyanuryl and hydrogen . $\Big\}$ $C_3H_6N_6 = N_3\Big\{\begin{matrix}Cy_3\\H_6\end{matrix}$

Secondary amides.—In these compounds, two-thirds of the hydrogen in a molecule of ammonia are replaced by acid radicals, viz.:

1. By two monatomic radicals; *e. g.*:—

Nitride of bisulphophenyl and hydrogen . . . . $\Big\}$ $C_{12}H_{11}NS_2O_4 = N\left\{\begin{matrix}C_6H_5SO_2\\C_6H_5SO_2\\H\end{matrix}\right.$

Nitride of sulphophenyl, benzoyl, and hydrogen . $\Big\}$ $C_{13}H_{11}NS_2O_4 = N\left\{\begin{matrix}C_6H_5SO_2\\C_7H_5O\\H\end{matrix}\right.$

These amides are produced by the action of acid chlorides on the primary amides or their metallic salts.

$$N\left\{\begin{matrix}C_6H_5SO_2\\H\\H\end{matrix}\right. + C_7H_5O . Cl = N\left\{\begin{matrix}C_6H_5SO_2\\C_7H_5O\\H\end{matrix}\right. + HCl.$$

2. The two atoms of hydrogen are replaced by one molecule of a biatomic radical. These compounds are called *imides*.

Carbonimide (cyanic acid) or nitride of carbonyl and hydrogen . . $\Big\}$ $CNHO = N\left\{\begin{matrix}CO\\H\end{matrix}\right.$

Succinimide, or nitride of succinyl and hydrogen . . . . . . $\Big\}$ $C_4H_5NO_2 = N\left\{\begin{matrix}C_4H_4O_2\\H\end{matrix}\right.$

Most of them are produced by the action of heat on the acid ammoniacal salts of bibasic acids, the change consisting in the elimination of 2 molecules of water:—

$$\underbrace{\left.\begin{matrix}C_4H_4O_2\\H\\NH_4\end{matrix}\right\}O_2}_{\text{Acid succinate of ammonia.}} - 2H_2O = \underbrace{N\left\{\begin{matrix}C_4H_4O_2\\H\end{matrix}\right.}_{\text{Succinimide.}};$$

by the action of heat on the biamides of bibasic acids, ammonia being then given off:—

$$\underbrace{N_2\left\{\begin{matrix}C_4H_4O_2\\H_2\\H_2\end{matrix}\right.}_{\text{Succinamide.}} - NH_3 = \underbrace{N\left\{\begin{matrix}C_4H_4O_2\\H\end{matrix}\right.}_{\text{Succinimide.}};$$

or by the action of heat on the amidogen acids.

Tertiary Amides.—In these compounds, all the hydrogen in ammonia is replaced by acid radicals.

α. Monatomic.—1. The hydrogen is replaced by three monatomic radicals; *e. g.*:—

Nitride of sulphophenyl, benzoyl, and acetyl . $N\left\{\begin{matrix}C_6H_5SO_2\\C_7H_5O\\C_2H_3O\end{matrix}\right.$

Nitride of sulphophenyl and benzoyl . . . . $N\left\{\begin{matrix}C_6H_5SO_2\\C_7H_5O\\C_7H_5O\end{matrix}\right.$

2. One atom of hydrogen is replaced by a monatomic, and the other two by a biatomic radical:—

Nitride of succinyl and sulphophenyl . . $N\left\{\begin{matrix}C_4H_4O_2\\C_6H_5SO_2\end{matrix}\right.$

These amides are formed by the action of acid chlorides on the secondary amides or their silver-salts.

3. All the hydrogen is replaced by a triatomic radical. The composition of several inorganic compounds may be expressed in this manner :—

Monophosphamide, or nitride of phosphoryl	=	$N . PO$.
Boramide, or nitride of boron	=	$N . B$.
Free nitrogen, or nitride of nitrogen, the amide of nitrous acid	=	$N . N$.
Protoxide of nitrogen, or nitride of azotyl, the amide of nitric acid . . .	=	$N . NO$.

β. Biatomic.—Compounds in which all the hydrogen of 2 molecules of ammonia is replaced by monatomic or biatomic radicals :—

Trisuccinamide, or biamide of trisuccinyl . $N_2\left\{\begin{matrix}C_4H_4O_2\\C_4H_4O_2\\C_4H_4O_2\end{matrix}\right.$

Biamide of succinyl, bibenzoyl, and bisulphophenyl . . . . $N_2\left\{\begin{matrix}C_4H_4O_2\\(C_7H_5O)_2\\(C_6H_5SO_2)_2\end{matrix}\right.$

These *tertiary biamides* are produced by the action of acid chlorides on other amides or biamides.

Intermediate nitrides, or *amidogen-salts.*—These are compounds in which the hydrogen of ammonia is replaced partly by a basic, partly by an acid radical. Most of the primary and secondary amides form such salts, which are produced by the direct action of the amides on the corresponding oxides or their salts ; *e. g.* :—

Benzamidate of mercury . . . . . $N\left\{\begin{matrix}C_7H_5O\\Hg\\H\end{matrix}\right.$

When the positive radical is an alcohol-radical, the compounds are called *alcalamides ;* those which contain phenyl, C_6H_5, are also called anilides : thus,—

Phenyl-acetamide or acetanilide . . $N\left\{\begin{matrix} C_6H_5 \\ C_2H_3O \\ H \end{matrix}\right.$

Ethyl-cyanamide . . . . $N\left\{\begin{matrix} C_2H_5 \\ Cy. \\ H \end{matrix}\right.$

Phosphides.—These compounds are derived from the type ammonia by the substitution of phosphorus for nitrogen, and of various radicals for the hydrogen. Phosphuretted hydrogen, PH_3, is analogous to ammonia, and forms with hydriodic acid a compound, $PH_3 . HI$, or PH_4I, which crystallises in cubes like iodide of ammonium, or iodide of potassium.

With the alcohol-radicals, phosphorus forms compounds analogous to the alcoholic nitrides, and like those bodies possessing alkaline properties; *e. g.*, triphosphomethylamine, or trimethyphosphine, $P(CH_3)_3$. These compounds may be obtained by the action of terchloride of phosphorus on zinc-methyl, zinc-ethyl, &c., the reaction being expressed by the following general equation:—

$$PCl_3 + 3C_nH_{2n+1}Zn = 3ZnCl + P(C_nH_{2n+1})_3.$$

These phosphides, treated with the iodides of the corresponding alcohol-radicals, yield compounds analogous to the ammonium bases: thus,—

$$P(CH_3)_3 + C_2H_5I = \left.\begin{matrix}(CH_3)_3 \\ C_2H_5\end{matrix}\right\}P . I.$$

The only negative or acid phosphide known is chloracetyphide, or phosphide of terchloracetyl $= P(C_2Cl_3O . H . H)$.

Arsenides and Antimonides.—Arsenic and antimony also form compounds of the ammonia type; *e. g.*, AsH_3; SbH_3; $As(C_2H_5)_3$; $Sb(C_2H_5)$; but the arsenides and antimonides of the alcohol-radicals differ considerably in their properties from the nitrides and phosphides, not combining with hydrochloric acid, &c., in the same manner as ammonia, but rather combining with oxygen, chlorine, iodine, &c., like metals. They belong, therefore, rather to the hydrogen type (p. 567).

HYDROGEN TYPE.

The primary derivatives of this type are: —

1. The *hydrides of the metals proper.* A small number only of these are known, viz., Cu_2H, AsH_3, and SbH_3. The two latter may also be regarded as derivatives of ammonia.

2. The *hydrides of the alcohol-radicals*, C_nH_{2n+1}, viz., marsh-gas, or hydride of methyl, $CH_4 = H\,.\,CH_3$; hydride of ethyl, $C_2H_6 = H\,.\,C_2H_5$; hydride of amyl, $C_5H_{12} = H\,.\,C_5H_{11}$, &c. These compounds are formed by the action of zinc on the chlorides or iodides of the corresponding alcohol-radicals: —

$$\underbrace{2C_2H_5I}_{\text{Iodide of ethyl.}} + Zn\,Zn = 2ZnI + \underbrace{H\,.\,C_2H_5}_{\text{Hydride of ethyl.}} + \underbrace{C_2H_4}_{\text{Ethylene.}};$$

also by the action of water on zinc-methyl, zinc-ethyl, &c.: —

$$Zn\,.\,C_2H_5 + \left.\begin{matrix}H\\H\end{matrix}\right\}O = H\,.\,C_2H_5 + \left.\begin{matrix}Zn\\H\end{matrix}\right\}O;$$

occasionally also in the destructive distillation or spontaneous decomposition of vegetable and animal substances. Marsh-gas, for example, is formed by the putrefaction of vegetable matter under water (I. 375). The hydrides of methyl and ethyl are gaseous at ordinary temperatures, the rest are liquid or solid. They are decomposed by chlorine, with formation of substitution-products; thus —

$$H\,.\,C_2H_5 + ClCl = H\,.\,C_2(H_4Cl) + HCl.$$

There are likewise hydrides of alcohol-radicals of the form $H\,.\,C_nH_{2n-7}$, the best known of which is benzol, or hydride of phenyl, C_6H_6 or $H\,.\,C_6H_5$. These compounds are obtained in the destructive distillation of many organic substances; benzol, for instance, by the distillation of coal. They are also formed by the dry distillation of the monobasic

acids $C_nH_{2n-9}O$, with excess of lime or baryta, a carbonate of the base being formed at the same time: —

$$\underbrace{C_7H_6O_2}_{\text{Benzoic Acid.}} = CO_2 + \underbrace{C_6H_6}_{\text{Benzol.}}.$$

3. The *hydrides of the aldehyde-radicals*, $C_n H_{2n-1}$. These are: —

Ethylene, olefiant gas, or hydride of acetosyl	$C_2H_4 = H . C_2H_3$
Propylene, or hydride of propionyl . . .	$C_3H_6 = H . C_3H_5$
Butylene, or hydride of butyryl	$C_4H_8 = H . C_4H_7$
Amylene, or hydride of valeryl . . .	$C_5H_{10} = H . C_5H_9$

These compounds might also be regarded as hydrides of the alcohol-radicals $C_n H_{2n-1}$; for example, propylene as hydride of allyl (p. 532). Possibly, however, there may be two isomeric series of these compounds, the one derived from the alcohols, the other from the aldehydes.

These hydro-carbons are formed by the destructive distillation of organic substances, several of them being found among the products of the distillation of coal. They are also produced by the action of strong sulphuric acid at a high temperature on the alcohols, the change consisting in the abstraction of the elements of water: thus: —

$$\underbrace{C_2H_6O}_{\text{Alcohol.}} - H_2O = \underbrace{C_2H_4}_{\text{Ethylene.}}.$$

The only body of the series which is gaseous at ordinary temperatures is ethylene (I. 384); the rest are liquid or solid. The first term, methylene, has not been obtained in the free state. These compounds are especially distinguished by combining with two atoms of chlorine, bromine, &c., forming compounds homologous with Dutch liquid or chloride of ethylene, $C_2H_4 . Cl_2$; whereas the hydrides of the radicals C_nH_{2n+1} are decomposed by chlorine.

The lower compounds of the series also combine with anhydrous sulphuric acid. Thus, olefiant gas is immediately

absorbed by the anhydrous acid, or by a coke ball soaked in fuming oil of vitriol. This property, and that of forming liquid compounds with chlorine and bromine, is made available for separating olefiant gas, and the other more volatile hydrocarbons of the series, from gaseous mixtures.

4. The hydrides of the acid radicals.

α. Monatomic.—The hydrides of the acid radicals $C_nH_{2n-1}O$, are evidently the aldehydes of the fatty acids (p. 535): thus:—

Acetic aldehyde $= H . C_2HO_3 = \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O$

Butyric aldehyde $= H . C_4H_7O = \left.\begin{matrix}C_4H_7\\H\end{matrix}\right\}O$

Benzoic aldehyde (bitter almond oil) $= H . C_7H_5O = \left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\}O$

The following compounds may be regarded as the aldehydes of monobasic mineral acids; that is to say, as the hydrides of the radicals contained in those acids considered as derivatives of water:—

Nitrous acid, or aldehyde of nitric acid $NHO_2 = H . NO_2$

Hydrochloric acid, or aldehyde of hypochlorous acid . . . . $ClH = H . Cl$

Hydrocyanic acid, or aldehyde of cyanic acid . . . . $CHN = H . Cy$

Spontaneously inflammable phosphuretted hydrogen, or aldehyde of hypophosphorous acid . . . . $PH = H . P$

β. Hydrides of biatomic acid radicals:—

Hydrosulphuric acid, or aldehyde of hyposulphurous acid . . . . . . $SH_2 = H_2 . S$

Hydroselenic acid, or aldehyde of hyposelenious acid . . . . $SeH_2 = H_2 . Se$

γ Hydrides of triatomic acid radicals:—

Non-spontaneously inflammable phosphuretted hydrogen, or aldehyde of phosphorous acid . . . . $PH_3 = H_3 . P$

Antimoniuretted hydrogen, or aldehyde of antimonious acid . . . . $SbH_3 = H_3 . Sb$

The secondary derivatives of the hydrogen-type are—

1. The ordinary metals:—Potassium, KK, derived from HH; antimony, SbSb, derived from H_3H_3; aluminium, Al_2Al_2, derived from H_3H_3, &c.

2. The *alcohol-metals,* derived from the type HH, both atoms of hydrogen being replaced by alcohol radicals. The only bodies of this class which have yet been obtained are those containing the radicals C_nH_{2n+1}; viz. (*a.*) Those in which the two atoms of hydrogen are replaced by the same radical: *methyl,* $CH_3 . CH_3$; *ethyl,* $C_2H_5 . C_2H_5$; *butyl* or *tetryl,* $C_4H_9 . C_4H_9$; *amyl,* $C_5H_{11} . C_5H_{11}$; *caproyl* or *hexyl,* $C_6H_{13} . C_6H_{13}$; and *capryl* or *octyl,* $C_8H_{17} . C_8H_{17}$.—(*b.*) Those in which the two atoms of hydrogen are replaced by different radicals: *ethylo-butyl, ethyl-amyl, methylo-caproyl, butyl-amyl, and butylo-caproyl.* The reasons for representing the bodies of the class (*a.*) in the free state, by the double formulæ, have been already given (p. 518).

These alcohol-metals are obtained by the action of zinc on the iodides of the alcohol-radicals (p. 531); by the action of sodium on the chlorides of the same radicals; and by the electrolysis of the alkaline salts of the fatty acids, carbonic acid and hydrogen being evolved at the same time:—

$$2\underbrace{\left(\left.\begin{matrix}CO.CH_3\\K\end{matrix}\right\}O\right)}_{\text{Acetate of potash.}} + H_2O = \underbrace{(CH_3)_2}_{\text{Methyl.}} + H_2 + CO_2 + \underbrace{\left.\begin{matrix}CO\\K_2\end{matrix}\right\}O_2}_{\text{Carbonate of Potash.}}$$

The alcohol-metals, containing two different radicals, are

obtained by the action of sodium on a mixture of the corresponding iodides: thus, with the iodides of ethyl and butyl—

$$\text{C}_2\text{H}_5\text{I} + \text{Na Na} = \text{NaI} + \text{NaC}_2\text{H}_5$$

and $$\text{C}_4\text{H}_9\text{I} + \text{NaC}_2\text{H}_5 = \text{NaI} + \text{C}_2\text{H}_5 . \text{C}_4\text{H}_9\text{;}$$

also, by the electrolysis of a mixture of the alkaline salts of two of the fatty acids.

Methyl and ethyl are gaseous at ordinary temperatures; the other alcohol-metals are liquids more or less volatile. They exhibit but little tendency to unite with other bodies. The alcohols and ethers cannot be formed from them directly. Oxygen and sulphur do not act upon them, and chlorine and bromine do not unite with them, but decompose them, forming substitution-products; they are not attacked by hydrochloric acid or by potash. For their boiling points and vapour-densities, see page 518.

3. Mixed metals, containing a metal proper and an alcohol-radical; *e. g. zinc-methyl*, $CH_3 . Zn$; *zinc-ethyl*, $C_2H_5 . Zn$; *zinc-amyl*, $C_5H_{11}Zn$; *stannethyl*, C_2H_5Sn; *arsenethyl*, $(C_2H_5)_3As$; *stibmethyl*, $(CH_3)Sb$, &c.

These compounds are obtained by the action of iodide of ethyl, &c., on the corresponding metals, or their alloys with potassium or sodium; thus, the compounds of ethyl and arsenic are obtained by distilling iodide of ethyl with arsenide of sodium; arsen-bimethyl or cacodyl, $(CH_3)_2As$, is likewise produced by the dry distillation of a mixture of acetate of soda and arsenious acid. To understand this reaction, it must be remembered that the radical of acetic acid, C_2H_3O, may be supposed to consist of CO conjugated with methyl, CH_3:—

$$4\underbrace{\left(\begin{matrix}\text{CO} . \text{CH}_3 \\ \text{Na}\end{matrix}\Big\}\text{O}\right)}_{\text{Acetate of soda.}} + \text{As}_2\text{O}_3 = \underbrace{\begin{matrix}(\text{CH}_3)_2\text{As} \\ (\text{CH}_3)_2\text{As}\end{matrix}\Big\}\text{O}}_{\text{Oxide of cacodyl.}} + 2\text{CO}_2 + 2\left(\begin{matrix}\text{CO} \\ \text{Na}_2\end{matrix}\Big\}\text{O}_2\right)$$

These compounds are liquids more or less volatile, and

generally having a very offensive odour; they oxidise rapidly in the air, and sometimes take fire. Zinc-methyl, zinc-ethyl, and cacodyl take fire instantly on coming in contact with the air.

Zinc-methyl, zinc-ethyl, and zinc-amyl differ in some respects from the other mixed metals in their behaviour with oxygen, sulphur, chlorine, iodine, &c. When these metals are exposed to the air, but not freely enough to cause them to take fire, they are converted into mixed ethers; thus,—

$$2\ (\rlap{-}\mathrm{C}\mathrm{H}_3 . \mathrm{Zn}) + \Theta\Theta = 2\left(\left.\begin{matrix}\rlap{-}\mathrm{C}\mathrm{H}_3\\ \mathrm{Zn}\end{matrix}\right\}\Theta\right).$$

Similarly with sulphur. Chlorine, bromine, and iodine, on the other hand, decompose them, producing a chloride of the metal and a chloride of the alcohol-radical:—

$$\rlap{-}\mathrm{C}\mathrm{H}_3 . \mathrm{Zn} + \mathrm{ClCl} = \rlap{-}\mathrm{C}\mathrm{H}_3 . \mathrm{Cl} + \mathrm{ZnCl}.$$

This difference of reaction is in perfect accordance with the bibasic character of oxygen and sulphur, and the monobasic character of chlorine, bromine, and iodine (compare pp. 515, 547). The same mixed metals decompose water, forming a hydrate of zinc and a hydride of the alcohol-radical:—

$$\rlap{-}\mathrm{C}\mathrm{H}_3\mathrm{Zn} + \left.\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right\}\Theta = \mathrm{H} . \rlap{-}\mathrm{C}\mathrm{H}_3 + \left.\begin{matrix}\mathrm{Zn}\\ \mathrm{H}\end{matrix}\right\}\Theta.$$

The other mixed metals—thence called conjugate metals—containing tin, antimony, arsenic, bismuth, lead, and mercury, combine as simple radicals with oxygen, chlorine, &c., forming oxides, chlorides, &c. The oxides of these conjugate metals may be regarded as derivatives of the oxides of the simple metals contained in them, one or more atoms of oxygen being replaced by its equivalent quantity of ethyl, &c.; that is, Θ by $(\rlap{-}\mathrm{C}_2\mathrm{H}_5)_2$, &c. This will be seen from the following table, in which the symbol Et stands for $(\rlap{-}\mathrm{C}_2\mathrm{H}_5)_2$:—

Type.		Derivative.
Arsenious acid, $As_2\Theta_3$	Oxide of arsen-biethyl	$As_2(Et_2\Theta)=\Theta\left\{\begin{matrix}As(C_2H_5)_2\\ As(C_2H_5)_2\end{matrix}\right.$
Arsenic acid, $As_2\Theta_5$	Oxide of arsen-triethyl	$As_2(Et_3\Theta_2)=\Theta_2\left\{\begin{matrix}As(C_2H_5)_3\\ As(C_2H_5)_3\end{matrix}\right.$
Arsenic acid, $As_2\Theta_5$	Oxide of arsenethylium	$As_2(Et_4\Theta)=\Theta\left\{\begin{matrix}As(C_2H_5)_4\\ As(C_2H_5)_4\end{matrix}\right.$
Stannic oxide, $Sn_2\Theta_2$	Oxide of stannethyl	$Sn_2(Et\Theta)=\Theta\left\{\begin{matrix}Sn(C_2H_5)\\ Sn(C_2H_5)\end{matrix}\right.$
Stannic oxide (2 at.), $Sn_4\Theta_4$	Oxide of $\frac{2}{3}$-stannethyl	$Sn_4(Et_3\Theta)=\Theta_2\left\{\begin{matrix}Sn_2(C_2H_5)_3\\ Sn_2(C_2H_5)_3\end{matrix}\right.$
Mercuric oxide (2 at.), $Hg_4\Theta_2$	Oxide of mercurethyl	$Hg_4(Et\Theta)=\Theta_2\left\{\begin{matrix}Hg_2(C_2H_5)\\ Hg_2(C_2H_5)\end{matrix}\right.$
Selenious acid (anhy.) (2 at.), $Se_2\Theta_4$	Oxide of selenethyl	$Se_2(Et_2\Theta_2)=\Theta_2\left\{\begin{matrix}Se(C_2H_5)_2\\ Se(C_2H_5)_2\end{matrix}\right.$
Nitric acid (anhyd.), $N_2\Theta_5$	Oxide of tetrethylium	$N_2(Et_4\Theta)=\Theta\left\{\begin{matrix}N(C_2H_5)\\ N(C_2H_5)\end{matrix}\right.$

The method of determining the equivalent in hydrogen of these conjugate radicals has been already explained (p. 526).

Acid metals, or *metalloids*.—These are the elements commonly called negative or chlorous: *e. g.* oxygen, sulphur, phosphorus, &c.

RELATIONS BETWEEN CHEMICAL COMPOSITION AND DENSITY.

*Atomic Volume of Liquids.**—The atomic volumes of bodies are the spaces occupied by quantities proportional to their atomic weights, and are calculated by dividing the atomic weights by the specific gravities (I. 210); thus, the atomic weights of copper and silver being, on the hydrogen scale, 31·7 and 108·1, and their specific gravities (water $=1$) being 8·93 and 10·57, their atomic volumes are, respectively, $\frac{31·7}{8·93}$

* H. Kopp, Ann. Ch. Pharm. xcvi. 2, 330.

and $\frac{108 \cdot 1}{10 \cdot 57}$, or 3·6 and 10·2. These numbers are, of course, only relative; their actual values depend on the units of atomic volume and density adopted.

It has already been observed, that the relations between atomic weight and density are much less simple in solids and liquids than in gases, the diversities in the rates of expansion by heat of liquid and solid bodies being alone sufficient to complicate these relations to a considerable extent. With regard to liquids in particular, the researches of Professor Kopp have shown that their atomic volumes are comparable only at temperatures for which the tensions of the vapours are equal; for example, at the boiling points of the liquids. If the atomic weights of liquids are compared with their densities at equal temperatures, no regular relations can be perceived; but when the same comparison is made at the boiling temperatures of the respective liquids, several remarkable laws become apparent. The density of a liquid at its boiling point cannot be ascertained by direct experiment; but when the density at any one point, say at 15·5° C. (60° F.), has been ascertained, and the rate of expansion is also known, the density at the boiling point may be calculated. Abundant data for these calculations are supplied by the labours of Kopp and Pierre (II. 433).

The following table contains Kopp's determinations of the atomic volumes of a considerable number of liquids containing carbon, hydrogen, and oxygen at their boiling points. The atomic weights are those of the hydrogen-scale. The *calculated* atomic volumes in the fourth column are determined by a method to be presently described; the *observed* atomic volumes in the fifth column are the quotients of the atomic weights, on the hydrogen-scale, divided by the specific gravities referred to water as unity.

Table A.

Atomic Volumes of Liquids containing Carbon, Hydrogen, and Oxygen.

Type	Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point. Calculated.	Observed.
Type HH.	Benzol	C_6H_6	78	99·0	96·0... 99·7 at 80°
	Cymol	C_5H_{14}	134	187·0	183·5...185·2 „ 175
	Naphthalin	$C_{10}H_8$	128	154·0	149·2 . . „ 218
	Aldehyde	$C_2H_4O_2$	44	56·2	56·0... 56·9 „ 21
	Valeraldehyde	$C_5H_{10}O_2$	86	122·2	117 3...120·3 „ 101
	Bitter almond oil	C_7H_6O	106	122·2	118·4 . . „ 179
	Cuminol	$C_{10}H_6O$	148	188·2	189·2 . . „ 236
	Butyl	C_3H_{16}	114	187·0	184·5...186·8 „ 108
	Acetone	C_3H_6O	58	78·2	77·3... 77·6 „ 56
Type HH.O.	Water	H_2O	18	18·8	18·8 . . „ 100
	Wood-spirit	CH_4O	32	40·8	41·9... 42·2 „ 59
	Alcohol	C_2H_6O	46	62·8	61·8... 62·5 „ 78
	Amylic alcohol	$C_5H_{12}O$	88	128·8	123 6...124·4 „ 135
	Phenylic alcohol	C_6H_6O	94	106·8	103·6...104·0 „ 194
	Benzoic alcohol	C_7H_8O	108	128·8	123·7 . . „ 213
	Formic acid	CH_2O_2	46	42 0	40·9... 41·8 „ 99
	Acetic acid	$C_2H_4O_2$	60	64·0	63·5... 63·8 „ 118
	Propionic acid	$C_3H_6O_2$	74	86·0	85·4 . . „ 137
	Butyric acid	$C_4H_8O_2$	88	108·0	106·4...107·8 „ 156
	Valerianic acid	$C_5H_{10}O_2$	102	130·0	130·2...131·2 „ 175
	Benzoic acid	$C_7H_6O_2$	122	130·0	126·9 . . „ 253
	Vinic ether	$C_4H_{10}O$	74	106·8	105·6...106·4 „ 34
	Acetic acid (anhydrous)	$C_4H_6O_3$	102	109·2	109·9...110·1 „ 138
	Formiate of methyl	$C_2H_4O_2$	60	64·0	63·4 . . „ 36
	Acetate of methyl	$C_3H_6O_2$	74	86·0	83·7... 85·8 „ 55
	Formiate of ethyl	$C_3H_6O_2$	74	86·0	84·9... 85·7 „ 55
	Acetate of ethyl	$C_4H_8O_2$	88	108·0	107·4...107·8 „ 74
	Butyrate of methyl	$C_5H_{10}O_2$	102	130·0	125·7...127·3 „ 93
	Propionate of ethyl	$C_5H_{10}O_2$	102	130·0	125·8 . . „ 93
	Valerate of methyl	$C_6H_{12}O_2$	116	152·0	148·7...149·6 „ 112
	Butyrate of ethyl	$C_6H_{12}O_2$	116	152 0	149·1...149·4 „ 112
	Acetate of butyl	$C_6H_{12}O_2$	116	152·0	149·3 . . „ 112
	Formiate of amyl	$C_6H_{12}O_2$	116	152·0	149·4...150·2 „ 112
	Valerate of ethyl	$C_7H_{14}O_2$	130	174·0	173·5...173·6 „ 131
	Acetate of amyl	$C_7H_{14}O_2$	130	174·0	173·3...175·5 „ 131
	Valerate of amyl	$C_{10}H_{20}O_2$	172	240·0	244·1 . . „ 188
	Benzoate of methyl	$C_8H_8O_2$	136	152·0	148·5...150·3 „ 190
	Benzoate of ethyl	$C_9H_{10}O_2$	150	174·0	172·4...174·8 „ 209
	Benzoate of amyl	$C_{12}H_{16}O_2$	192	240·0	247·7 . . „ 266
	Cinnamate of ethyl	$C_{11}H_{12}O_2$	176	207·0	211·3 . . „ 260
Type 2(HH.O).	Acid salicylate of methyl	$C_8H_8O_3$	152	159·8	156·2...157·0 „ 223
	Carbonate of ethyl	$C_5H_{10}O_3$	118	137·8	138·8...139·4 „ 126
	Oxalate of methyl	$C_4H_6O_4$	118	117·0	116·3 . . „ 162
	Oxalate of ethyl	$C_6H_{10}O_4$	146	161·0	166·8...167·1 „ 186
	Succinate of ethyl	$C_8H_{14}O_4$	174	205·0	209·0 . . „ 217

A comparison of the numbers in this table leads to the following remarkable results: —

1. *Differences of atomic volume are in numerous instances proportional to the differences between the corresponding chemical formulæ.*—Thus liquids, whose formulæ differ by $n . CH_2$, differ in atomic volume by $n . 22$; for example, the atomic volumes of formiate of methyl, $C_2H_4O_2$, and butyrate of ethyl, $C_6H_2O_2$, differ by nearly 4×22. Acetate of ethyl, $C_4H_8O_2$, and butyrate of methyl, $C_5H_{10}O_2$, whose formulæ differ by CH_2, differ in atomic volume by nearly 22. The same law holds good with respect to liquids containing sulphur, chlorine, iodine, bromine, and nitrogen (see Tables B, C, D). Again: by comparing the atomic volumes of analogous chlorine and bromine compounds, it is found that the substitution of 1, 2, or 3 atoms of bromine for an equivalent quantity of chlorine, increases the atomic volume of a compound by once, twice, or three times 5. This will be seen by comparing the atomic volumes of PBr_3 and PCl_3; C_2H_5Br and C_2H_5Cl, &c. (Table C.)

2. *Isomeric liquids belonging to the same chemical type have equal atomic volumes.*—The atomic volume of acetic acid, $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$, is between 63·5 and 63·8; that of formiate of methyl, $\left.\begin{matrix}CHO\\CH_3\end{matrix}\right\}O$, is 63·4; the atomic volume of butyric acid, $\left.\begin{matrix}C_4H_7O\\H\end{matrix}\right\}O$, is between 106·4 and 107·8; that of acetate of ethyl, $\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O$, is between 107·4 and 107·8.

3. *In liquids of the same chemical type, the replacement of hydrogen by an equivalent quantity of oxygen* (that is to say, of 1 pt. of hydrogen by 8 pts. of oxygen) *makes but a slight alteration in the atomic volume.*—This may be seen by comparing the atomic volumes of alcohol, C_2H_6O, and acetic acid, $C_2H_4O_2$; of ether, $C_4H_{10}O$, acetate of ethyl, $C_4H_8O_2$, and anhydrous acetic acid, $C_4H_6O_3$; of cymol, $C_{10}H_{14}$, and

cuminol, $C_{10}H_{12}Ɵ$. The alteration caused by the substitution of $Ɵ$ for H_6 is always an increase.

4. *In liquids of the same chemical type, the replacement of* 2 *at.* H *by* 1 *at.* Ꞓ (1 pt. by weight of hydrogen by 6 parts of carbon) *makes no alteration in the atomic volume.*—Such, for example, is the case with benzoate of ethyl, $Ꞓ_9H_{10}Ɵ_2$, and valerate of ethyl, $Ꞓ_7H_{14}Ɵ_2$, and with the corresponding benzoates and valerates in general; also with bitter almond oil, $Ꞓ_7H_6Ɵ$, and valeraldehyde, $Ꞓ_5H_{10}Ɵ$.

In liquids belonging to different types, the same relations are not found to hold good. Moreover, the types within which these relations are observed, are precisely those of Gerhardt's classification (II. 528). Further, when liquid compounds are represented by rational formulæ founded on these types, their atomic volumes may be calculated from certain fundamental values of the atomic volumes of the elements, on the supposition that the atomic volume of a liquid compound is equal to the sum of the atomic volumes of its constituent elements.

Since the addition of $ꞒH_2$ to a compound increases the atomic volume by 22, this number may be taken to represent the atomic volume of $ꞒH_2$; moreover, since Ꞓ (or C_2) may take the place of H_2 in combination, without altering the atomic volume of the compound, it follows that the atomic volume of Ꞓ must be equal to that of H_2; and therefore the atomic volume of $Ꞓ = \frac{22}{2} = 11$, and that of H_2 also equal to 11, or that of $H = 5{\cdot}5$. Further, as the substitution of $Ɵ$ for H_2 produces a slight increase in the atomic volume of a compound, the atomic volume of $Ɵ$ must be rather greater than 11; and it is found that, by assuming the atomic volume of $Ɵ$, when it takes the place of H_2 (that is to say, in a radical, as when acetyl, $Ꞓ_2H_3Ɵ$, is formed from ethyl, $Ꞓ_2H_5$), to be equal to 12·2, results are obtained agreeing very nearly with those of observation. But when oxygen occupies the

position which it has in water, $\begin{matrix}H\\H\end{matrix}\!\!\Theta$, its atomic volume is smaller. The specific gravity of water at the boiling point is 0·9579; hence its atomic volume at that temperature is $\frac{18}{0 \cdot 9579} = 18 \cdot 8$; now the 2 atoms of hydrogen occupy a space equal to 11; hence the volume of the oxygen is 7·8. The same value of the atomic volume substituted for Θ in the formulæ of the several compounds belonging to the water-type, in which it occupies a similar place, that is to say, outside the radical, gives results agreeing nearly with observation. That a given quantity of a substance should occupy different spaces, under different circumstances, is a fact easily explained, when it is remembered that the particles of a body cannot be supposed to be in absolute contact, but are separated by certain spaces, which increase or diminish according to the temperature of the body, and according as it is in the solid, liquid, or gaseous state.

From these values of the atomic volumes of the elements carbon, hydrogen, and oxygen; viz. —

Atomic volume of	$\mathrm{C}\!\!\!-$	. . . . =	11
,, ,,	H	. . . . =	5·5
,, ,,	Θ (within the radical)	=	12·2
,, ,,	Θ (without the radical)	=	7·8;

the calculated values of the atomic volumes of liquids, in the fourth column of Table A, are deduced. The method of calculation may be understood from the following examples:

Benzol, $\mathrm{C}\!\!\!-_6H_6 = \mathrm{C}\!\!\!-_6H_5 . H.$

Atomic volume of	$\mathrm{C}\!\!\!-_6$	. . . . =	66
,, ,,	H_6	. . . . =	33
,, ,,	benzol	. . . =	99

Aldehyde, $C_2H_4O = C_2H_3O \cdot H$.

Atomic volume of C_2	= 22
" " H_4	= 22
" " O (within the radical)	= 12·2
" " aldehyde . . .	= 56·2

Alcohol, $C_2H_6O = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$.

Atomic volume of C_2	= 22
" " H_6	= 33
" " O (without the radical)	= 7·8
" " alcohol . . .	= 62·8

Acetic acid, $C_2H_4O_2 = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$.

Atomic volume of C_2	= 22
" " H_4	= 22
" " O (within the radical)	= 12·2
" " O (without the radical)	= 7·8
" " acetic acid . . .	= 64·0

Anhydrous acetic acid, $C_4H_6O_3 = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$.

Atomic volume of C_4	= 44
" " H_6	= 33
" " O_2 (within the radical)	= 24·4
" " O (without the radical)	= 7·8
" " anhydrous acetic acid .	= 109·2

Oxalate of methyl, $C_4H_6O_4 = \left.\begin{matrix}C_2O_2\\(CH_3)_2\end{matrix}\right\}O_2$.

Atomic volume of C_4	= 44
" " H_6	= 33
" " O_2 (within the radical)	= 24·4
" " O_2 (without the radical)	= 15·6
" " oxalate of methyl .	= 117·0

Liquids containing Sulphur.—Sulphur enters into combination in various ways; sometimes taking the place of oxygen in the type $HH.O$ (as in mercaptan); sometimes taking the place of carbon within a radical (as in anhydrous sulphurous acid) $SO.O$, compared with anhydrous carbonic acid $CO.O$; sometimes replacing oxygen within a radical (as in sulphide of carbon), $CS.S$, compared with anhydrous carbonic acid. In the first and second cases, the atomic volume of sulphur-compounds may be calculated by attributing to sulphur ($S = 32$), the atomic volume 22·6, those of the other elements remaining as above; in the third case, the atomic volume of sulphur appears to be greater; viz., 28·6.

Examples.—*Mercaptan*, $C_2H_6S = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$.

Atomic volume of C_2	= 22
„ „ H_6	= 33
„ „ S	= 22·6
„ „ mercaptan . . .	= 77·6

Sulphide of carbon, $CS_2 = CS{\cdot}S$.

Atomic volume of C	= 11
„ „ S (within the radical)	= 28·6
„ „ S (without the radical)	= 22·6
„ „ sulphide of carbon .	= 62·2

TABLE B.

Atomic Volumes of Liquid Sulphur-compounds.

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point. Calculated.	Observed.
Mercaptan . . .	C_2H_6S	62	77·6	76·0... 76·1 at 36° C.
Amylic mercaptan .	$C_5H_{12}S$	104	143·6	140·1...140·5 „ 120
Sulphide of methyl .	C_2H_6S	62	77·6	75·7 . . „ 41
Sulphide of ethyl . .	$C_4H_{10}S$	90	121·6	120·5...121·5 „ 91
Bisulphide of methyl .	$C_2H_6S_2$	94	100·2	100·6...100·7 „ 114
Sulphurous acid . .	SO_2	64	42·6	43·9 . . „ −8
Sulphite of ethyl . .	$C_4H_{10}SO_3$	138	149·4	148·8...149·5 „ 160
Bisulphide of carbon .	CS_2	76	62·2	62·2... 62·4 „ 47

Chlorides, Bromides, and Iodides.—In liquid compounds of this class, the atomic volume of Cl is supposed to be 22·8, that of Br = 27·8, and that of I = 37·5, those of the other elements remaining as above.

TABLE C.

Atomic Volumes of Liquid Chlorides, Bromides, and Iodides.

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point. Calculated.	Observed.
Bichlorinated ethylene .	$C_2H_2Cl_2$	97	78·6	79·9 . . at 37° C.
Chloride of carbon .	C_2Cl_4	166	113·2	115·4 . . „ 123
Chloride of ethylene .	$C_2H_4Cl_2$	99	89·6	85·8... 86·4 „ 85
———, monochlorinated	$C_2H_3Cl_3$	133·5	106·9	105·4...107·2 „ 115
———, bichlorinated .	$C_2H_2Cl_4$	168	124·2	120·7...121·4 „ 137
———, terchlorinated .	C_2HCl_5	202·5	141·5	143 . . „ 154
Chloride of butylene .	$C_4H_8Cl_2$	127	133·6	129·5...133·7 „ 123
Monochlorinated chloride of methyl . . .	CH_2Cl_2	85	67·6	64·5 . . „ 30·5
Chloroform . . .	$CHCl_3$	119·5	84·9	84·8... 85·7 „ 62
Chloride of carbon .	CCl_4	154	102·2	104·3...107·0 „ 78
Chloride of ethyl . .	C_2H_5Cl	64·5	72·3	71·2... 74·5 „ 11
———, monochlorinated	$C_2H_4Cl_2$	99	89·6	86·9... 89·9 „ 64
———, bichlorinated .	$C_2H_3Cl_3$	133·5	106·9	105·6...109·7 „ 75
Chloride of amyl . .	$C_5H_{11}Cl$	106·5	138·3	135·4...137·0 „ 102
Chloral . . .	C_2HCl_3O	147·5	108·1	108·4...108·9 „ 96
Chloride of acetyl . .	C_2H_3OCl	78·5	73·5	74·4... 75·2 „ 55
Chloride of benzoyl .	C_7H_5OCl	140·5	139·5	134·2...137·8 „ 198
Bromine . . .	Br_2	160	55·6	54 ... 57·4 „ 63
Bromide of methyl .	CH_3Br	95	55·3	58·2 . . „ 13
Bromide of ethyl . .	C_2H_5Br	109	77·3	78·4 . . „ 41
Bromide of amyl . .	$C_5H_{11}Br$	151	143·3	149·2 . . „ 119
Bromide of ethylene .	$C_2H_4Br_2$	188	99·6	97·5... 99·9 „ 130
Iodide of methyl . .	CH_3I	142·1	65·0	65·4... 68·3 „ 43
Iodide of ethyl . .	C_2H_5I	156·1	87·0	85·9... 86·4 „ 71
Iodide of amyl . .	$C_5H_{11}I$	198·1	153·0	152·5...155·8 „ 147
Chloride of sulphur .	SCl	67·5	. .	45·7 . . „ 140
Chloride of phosphorus .	PCl_3	137·5	. .	93·9 . . „ 78
Bromide of phosphorus .	PBr_3	271	. .	108 6 . . „ 175
Chloride of silicon .	$SiCl_3$	127·8	. .	91·6 . . „ 59
Bromide of silicon .	$SiBr_3$	261·3	. .	108·2 . . „ 153
Chloride of arsenic .	$AsCl_3$	181·5	. .	94·8 . . „ 133
Chloride of antimony .	$SbCl_3$	235 5	. .	100·7 . . „ 223
Bromide of antimony .	$SbBr_3$	369	. .	116·8 . . „ 275
Chloride of tin . .	$SnCl_2$	129	. .	65·7 . . „ 115
Chloride of titanium .	$TiCl_2$	96	. .	63·0 . . „ 136

The compounds PCl_3, $SiCl_3$, and $AsCl_3$ have nearly equal atomic volumes, whence it may be inferred that phosphorus, silicon, and arsenic, in their liquid compounds, have equal atomic volumes. The same conclusion may be drawn regarding tin and titanium, since the atomic volumes of $SnCl_2$ and $TiCl_2$ are equal.

Nitrogen-compounds. — In compounds belonging to the ammonia type, the atomic volume of nitrogen is 2·3. This result is deduced from the observed atomic volume of aniline, Ꞓ_6H_7N, which is 106·8. Now the atomic volume of $6\,\text{Ꞓ} + 7\,H = 6 \,.\, 11 + 7 \,.\, 5{\cdot}5 = 104{\cdot}5$, which number, deducted from 106·8, leaves 2·3 for the atomic volume of nitrogen.

The atomic volume of cyanogen deduced from the observed at. vol. of cyanide of phenyl, $\text{Ꞓ}N \,.\, \text{Ꞓ}_6H_5$, or Ꞓ_7H_5N, is nearly 28. Thus—

Atomic volume of		Ꞓ_7H_5N	=	121·6
„	„	Ꞓ_6H_5	=	93·5
„	„	$\text{Ꞓ}N$	=	28·1

A similar calculation, founded on the observed atomic volume of cyanide of methyl, Ꞓ_2H_3N, gives, for the at. vol. of cyanogen, the number 26·8. The atomic volume of liquid cyanogen determined directly at 37° or 39° C. above its boiling point, is between 28·9 and 30·0. As a mean of these values, the atomic volume of cyanogen may be assumed to be 28; and with this value the atomic volumes of the liquid cyanides are calculated. Thus, for

Oil of mustard (sulpho-cyanide of allyl), $\text{Ꞓ}_4H_5N\text{S̶} = \left.\begin{matrix}\text{Ꞓ}N \\ \text{Ꞓ}_3H_5\end{matrix}\right\}\text{S̶}$.

Atomic volume of		Ꞓ_3H_5 . . .	=	60·5
„	„	$\text{Ꞓ}\,N$ . . .	=	28·0
„	„	S̶ (without the radical)	=	22·6
„	„	oil of mustard . .	=	111·1

The atomic volumes of compounds containing the radical NO_2 are calculated on the hypothesis that the at. vol. of that radical is 33, which agrees nearly with the observed atomic volume of liquid peroxide of nitrogen. Thus:—the at. vol. of nitrite of amyl, $C_5H_{11}NO_2$ = at. vol. of C_5H_{11} + at. vol. of NO_2 = 115·5 + 33 = 148·5.

TABLE D.

Atomic Volumes of Liquids containing Nitrogen.

Substance.	Formula.	Atomic Weight.	Atomic Volume at the Boiling Point.	
			Calculated.	Observed.
Ammonia	H_3N	17	18·8	22·4... 23·3 at 10°...16°*
Ethylamine	C_2H_7N	45	62·8	65·3 . . . at 18·7
Butylamine	$C_4H_{11}N$	73	106·8	
Amylamine	$C_5H_{13}N$	87	128·8	125·0 . . . . „ 94
Caprylamine . . .	$C_8H_{19}N$	129	194·8	190·0 . . . . „ 170
Aniline	C_6H_7N	93	106·8	106·4...106·8 . „ 184
Toluidine	C_7H_9N	107	128 8	
Ethaniline	$C_8H_{11}N$	121	150·8	150·6 . . . . „ 204
Biethaniline	$C_{10}H_{15}N$	149	194·8	190·5 . . . . „ 213·5
Cyanogen	CN	26	28·0	28·9... 30·0 . „ 16†
Hydrocyanic acid . .	CHN	27	33·5	39·1 . . . . „ 27
Cyanide of methyl .	C_2H_3N	41	55·5	54·3 . . . . „ 74
Cyanide of ethyl . .	C_3H_5N	55	77·5	77·2 . . . . „ 88
Cyanide of butyl . .	C_5H_9N	83	121·5	
Cyanide of phenyl . .	C_7H_5N	103	121·5	121·6...121·9 . „ 191
Sulphocyanide of methyl	C_2H_3NS	73	78·1	75·2... 78·2 . „ 133
Sulphocyanide of ethyl .	C_3H_5NS	87	100·1	99·1 . . . . „ 146
Oil of mustard . .	C_4H_5NS	99	111·1	113 1...114·2 . „ 148
Cyanate of ethyl . .	C_3H_5NO	71	85·3	84·3... 84·8 . „ 60
Peroxide of nitrogen .	NO_3	30	33·0	31·7... 32·4 . „ 40‡
Nitrate of methyl . .	CH_3NO_3	77	68·3	69·4 . . . . „ 66
Nitrate of ethyl . .	$C_2H_5NO_3$	101	90·3	90·0... 90·1 . „ 86
Nitrobenzol . . .	$C_6H_5NO_2$	123	126·5	122·6...124·9 . „ 218
Nitrite of methyl . .	CH_3NO_2	61	60·5	61·6 . . . . „ 14§
Nitrite of ethyl . .	$C_2H_5NO_2$	75	82·5	79·2... 84·6 . „ 18
Nitrite of amyl . .	$C_5H_{11}NO_2$	117	148·5	148·4 . . . . „ 95

* Between 44° and 50° above the boiling point.

† Between 37° and 39° above the boiling point.

‡ About 35° above the boiling point.

§ 27° above the boiling point.

From the preceding observations and calculations, it appears that the atomic volume of a compound depends, not merely on its empirical, but likewise on its rational formula; in other words, not merely on the number of atoms of its elements, but further on the manner in which those atoms are arranged. Now it has been shown (p. 522) that a compound may have more than one rational formula, according to the manner in which it decomposes; and hence it might appear that the calculation of atomic volumes must be attended with considerable uncertainty, inasmuch as the atomic volumes of certain elements, as oxygen and sulphur, vary according to the manner in which they enter into the compound. Aldehyde, for example, may be represented either as $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O$, or as $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}$; and, as the atomic volume of oxygen is 12·2 or 7·8, according as it is within or without the radical, the atomic volume of aldehyde will be 56·2 if deduced from the type HH, and 51·8 if deduced from the type HH . O. But the atomic weight of aldehyde, and its specific gravity at a given temperature are invariable; it cannot, therefore, have two different atomic volumes. It must be remembered, however, that, in speaking of a compound as having several rational formulæ, we consider it rather in a dynamical than in a statical point of view; as under the influence of disturbing forces, and on the point of undergoing chemical change. But if, on the other hand, we regard a compound in its fixed statical condition, as a body possessing definite physical properties, a certain specific gravity, a certain boiling point, rate of expansion, refractive power, &c., we can scarcely avoid attributing to it a fixed molecular arrangement, or, at all events, supposing that the disposition of its atoms is confined within those limits which constitute chemical types. It is found, indeed, that isomeric liquids exhibit equal atomic volumes only when they belong to the same chemical type. If this view be correct, the relation

between the atomic volumes of elements and compounds, may often render valuable service in determining the rational formula which belongs to a compound in the state of rest. Thus, of the two atomic volumes just calculated for aldehyde, the number 56·2, deduced from the formula $C_2H_3O \,.\, H$, agrees with the observed atomic volume of aldehyde, which is between 56·0 and 56·9, better than 51·8, the number deduced from $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O$. This result leads to the conclusion that the aldehydes belong to the hydrogen-type (p. 565), rather than to the water-type.

There are many groups of liquid compounds, irrespective of isomerism or similarity of type, the members of which have equal or nearly equal atomic volumes. The following table exhibits the calculated atomic volumes of several of these groups:—

Atomic Volume of Liquids.

Water	H_2O	18·8	Ether	$C_4H_{10}O$	106·8
Ammonia	NH_3	18·8	Butylic alcohol	$C_4H_{10}O$	106·8
			Phenylic alcohol	C_6H_6O	106·8
Bromine	Br_2	55·6	Butylamine	$C_4H_{11}N$	106·8
Cyanogen	$(CN)_2$	56·0	Aniline	C_6H_7N	106·8
Aldehyde	C_2H_4O	56·2	Butyric acid	$C_4H_8O_2$	108·0
Cyanide of methyl	C_2H_3N	55·5	Acetate of ethyl	$C_4H_8O_2$	108·0
Bromide of methyl	C_2H_3Br	55·3	Anhydrous acetic acid	$C_4H_6O_3$	109·2
			Chloral	C_2HClO	108·1
Alcohol	C_2H_6O	62·8	Bichlorinated chloride of ethyl	$C_2H_3Cl_3$	106·9
Acetic acid	$C_2H_4O_2$	64·0			
Formiate of methyl	$C_2H_4O_2$	64·0	Monochlorinated chloride of ethylene	$C_2H_3Cl_3$	106·9
Cyanate of methyl	$C_2H_3NO_2$	63·3			
Ethylamine	C_2H_7N	62·8	Bromide of phosphorus	PBr_3	108·6
Sulphide of carbon	CS_2	62·3			
Iodide of methyl	CH_3I	65·0			
			Valeraldehyde	$C_5H_{10}O$	122·2
Acetone	C_3H_6O	78·2	Cyanide of butyl	C_5H_9N	121·5
Cyanide of ethyl	C_3H_5N	77·5	Bitter almond oil	C_7H_6O	122·2
Sulphocyanide of methyl	C_2H_3NS	78·1	Cyanide of phenyl	C_7H_5N	121·5
Sulphide of methyl	C_2H_6S	77·6	Sulphide of ethyl	$C_4H_{10}S$	121·6

These groups exhibit an approach to the uniformity of atomic volume which is observed in the gaseous state.

Berthelot has adduced a number of examples, showing that

when a liquid compound is formed by the union of two other liquids, whose specific volumes are denoted by A and B, with elimination of x atoms of water, the specific volume of the compound is nearly $= A + B - xC$ (the atomic volume of water being denoted by C). Berthelot's observations, however, were made at medium temperatures, not at the boiling points of the liquids.

Atomic Volume of Solids.—The principal results obtained by Kopp, with reference to the atomic volume of solid bodies, are given in Vol. I. pp. 210—216.* The difficulty of reducing the results to general laws is similar to that which has been noticed in the case of liquids, but exists to a still greater extent, inasmuch as our knowledge of the expansion of solids by heat is much more limited than that of liquids. It is probable that the atomic volumes of solids should be compared at their melting points; since it is only at those temperatures that the effects of heat upon different solids can be said to be equal. Now the specific gravities of most solids are determined only at medium temperatures, from which the melting points of different solids are separated by intervals of very different magnitude; moreover, there are but few solids whose rate of expansion at different temperatures has been ascertained with sufficient accuracy to render it possible to calculate the specific gravities at the melting points. A further complication arises from the different densities which the same solid often exhibits, according as it is amorphous or crystalline, or according to the particular form in which it crystallises.

* The numbers there given refer to the oxygen-scale of atomic weights. (O = 100.)

RELATIONS BETWEEN CHEMICAL COMPOSITION AND BOILING POINT.*

In compounds of similar constitution, and especially among the members of homologous series (p. 532), difference of boiling point is frequently proportional to difference of composition.

1. In the alcohols, $C_nH_{2n+2}O$, the fatty acids, $C_nH_{2n}O_2$, and the compound ethers (p. 545) isomeric with the fatty acids, a difference of CH_2 in the formula corresponds to a difference of 19° C. in the boiling point.

2. The boiling point of a fatty acid, $C_nH_{2n}O_2$, is higher by 40° C. than that of the corresponding alcohol, $C_nH_{2n+2}O$.

3. The boiling point of a compound ether, $C_nH_{2n}O_2$, is lower by 82° C. than that of the isomeric acid.

Starting from the observed boiling point of common alcohol, 78° C., and calculating by these rules the boiling points of the other alcohols and of the fatty acids and ethers, we obtain the numbers in the third column of the following table, which do not differ from the observed boiling points in the fourth column, more than these latter, as determined by different observers, differ from one another.

Substance.	Formula.	Boiling point. Calculated.	Boiling point. Observed.	Observers.
Alcohols.				
Methylic alcohol .	CH_4O	59°	60° . . at 744 mm.	Kane.
			61 . . „ 755 „	Delffs.
			64·9 . . „ 754 „	H. Kopp.
			65 . . „ 752 „	H. Kopp.
Propylic alcohol .	C_3H_8O	97	96 . . „ ? „	Chancel.
Butylic alcohol .	$C_4H_{10}O$	116	109 . . „ ? „	Wurtz.
Amylic alcohol .	$C_5H_{12}O$	135	130·4 . . „ 742 „	H. Kopp.
			132 . . „ 760 „	Cahours.
			132 . . „ 766 „	Delffs.
Cetylic alcohol .	$C_{16}H_{34}O$	344	360 . . „ ? „	Favre and Silbermann.

* H. Kopp. Ann. Ch. Pharm. xcvi. 2, 330.

Substance.	Formula.	Boiling point.		Observed.
		Calculated.	Observed.	
Acids.				
Formic acid . .	CH_2O_2	99	98·5 . . at 753 mm.	Liebig.
			105·4 . . „ 764 „	H. Kopp.
Acetic acid . .	$C_2H_4O_2$	118	116·9 . . „ 750 „	H. Kopp.
			116 . . „ 754 „	Delffs.
Propionic acid .	$C_3H_6O_2$	137	141·6 . . „ 754·6 „	H. Kopp.
			141 . . „ ? „	Limpricht and v. Uslar.
Butyric acid . .	$C_4H_8O_2$	156	156 . . „ 733 „	H. Kopp.
			163 . . „ 751 „	I. Pierre.
Valerianic acid .	$C_5H_{10}O_2$	175	174·5 . . „ 762 „	Delffs.
			175·8 . . „ 746·5 „	H. Kopp.
Caproïc acid . .	$C_6H_{12}O_2$	194	198 . . „ ? „	Brazier and Gossleth.
Caprylic acid . .	$C_8H_{16}O_2$	232	236 . . „ ? „	Fehling.
Pelargonic acid .	$C_9H_{18}O_2$	251	260 . . „ ? „	Cahours.
Compound Ethers.				
Formiate of methyl.	$C_2H_4O_2$	36	32·7 . . „ 741 „	H. Kopp.
			22·9 . . „ 752 „	Andrews.
Acetate of methyl .	$C_3H_6O_2$	55	55 . . „ 762 „	Andrews.
			55·7 . . „ 757 „	H. Kopp.
			59·5 . . „ 761 „	I. Pierre.
Formiate of ethyl .	$C_3H_6O_2$	55	52·9 . . „ 752 „	I. Pierre.
			53 . . „ 736 „	Delffs.
			54·7 . . „ 754 „	H. Kopp.
Acetate of ethyl .	$C_4H_8O_2$	74	73·7 . . „ 745 „	H. Kopp.
			74·1 . . „ 766 „	I. Pierre.
Butyrate of methyl.	$C_5H_{10}O_2$	93	93 . . „ 744 „	Delffs.
			95·1 . . „ 742 „	H. Kopp.
			102·1 . . „ 744 „	I. Pierre.
Acetate of propyl .	$C_5H_{10}O_2$	93	90 (about)	Berthelot.
Propionate of ethyl.	$C_5H_{10}O_2$	93	95·8... 98 . „	H. Kopp.
Valerate of methyl.	$C_6H_{12}O_2$	112	114 ...115 „ 756 „	H. Kopp.
Butyrate of ethyl .	$C_6H_{12}O_2$	112	114·6 . . „ 756 „	H. Kopp.
			119 . . „ 747 „	I. Pierre.
Formiate of amyl .	$C_6H_{12}O_2$	112	114 . . „ 771 „	Delffs.
			116 (about)	H. Kopp.
Acetate of butyl .	$C_6H_{12}O_2$	112	114	Wurtz.
Valerate of ethyl .	$C_7H_{14}O_2$	131	131·3 . . „ 735 „	Delffs.
			133·2 . . „ 754 „	H. Kopp.
Acetate of amyl .	$C_7H_{14}O_2$	131	133 . . „ 760 „	Delffs.
			133·3 . . „ 749 „	H. Kopp.
			137·6 . . „ 746 „	H. Kopp.
Valerate of amyl .	$C_{10}H_{20}O^2$	188	187·8...188·3 „ 730 „	H. Kopp.

It appears from this table that isomeric compound ethers have equal boiling points, *e.g.* formiate of ethyl and acetate of

methyl boil at 55°; valerate of methyl, butyrate of ethyl, formiate of amyl, and acetate of butyl, boil at 112°. It follows, also, from the preceding laws, that the boiling point of an acid, $C_nH_{2n}O_2$, is 63° higher than that of its methylic ether, 44° higher than that of its ethylic ether, and 13° lower than that of its amylic ether: thus, valerianic acid boils at 175°; valerate of methyl at 112°; valerate of ethyl at 131°; valerate of amyl at 188°. Common ether, $(C_2H_5)_2O$, is the ethyl-salt of alcohol, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$, regarded as an acid; that is to say, it bears the same relation to alcohol that acetate of ethyl bears to acetic acid: hence its boiling point should be $78° - 44° = 34°$. The actual observations of the boiling point of ether vary from 34° to 35·7°.

In the same series of homologous compounds, it is found that the addition of n C raises the boiling point by $n \,.\, 29°$; and the addition of n H lowers the boiling point by $n \,.\, 5°$ [consequently, the addition of nCH_2 raises it by $n \,.\, (29 - 2 \times 5) = n \,.\, 19°$]. The same law is likewise observed in other series of compounds of similar character. Thus, benzoate of ethyl, $C_9H_{10}O_2$, boils at 209°, which is higher by 4×29, or 116, than the boiling point of the ethers $C_5H_{10}O_2$,—butyrate of methyl for example. The boiling point of angelic acid, $C_5H_8O_2$, is higher by 29° than that of butyric acid, $C_4H_8O_2$; and 2×5, or 10°, higher than that of valerianic acid, $C_5H_{10}O_2$. The boiling point of phenylic alcohol, C_6H_6O, is higher by about 4×29, or 116°, than that of common alcohol, C_2H_6O; and about 8×5, or 40°, higher than that of caproic alcohol, $C_6H_{14}O$.

Constant relations of composition and boiling point are observed also in other series of homologous compounds; but the difference of boiling point corresponding with a difference of CH_2, is not always 19°. In the series of hydrocarbons:—benzol, C_6H_6 (B.P. 80°), toluol, C_7H_8, xylol, C_8H_{10}, cumol, C_9H_{12}, cymol, $C_{10}H_{14}$, the difference is 24°; in the homologous

compounds:—bromide of ethylene, $C_2H_4Br_2$, bromide of propylene, $C_3H_6Br_2$, bromide of butylene, $C_4H_8Br_2$, it is 15°, their boiling points being 130°, 145°, and 160°, respectively. In the series of alcohol-radicals (in the free state), the difference is about 23°; in the anhydrous acids, homologous with anhydrous acetic acid, it is about 13°.

These differences of boiling point would probably be the same in all series of homologous compounds, if the boiling points were determined at different pressures. It is not, indeed, to be expected that two substances should exhibit the same difference of boiling point under all pressures; for if B and B′ denote the boiling points of two liquids at the ordinary atmospheric pressure, b and b′, the boiling points of the same liquids at another pressure; and if we suppose that

$$B - B' = b - b',$$

it will follow that

$$B - b = B' - b';$$

that is to say, the boiling points of the two liquids would vary equally for equal differences of pressure, which is contrary to observation.

CHEMICAL AFFINITY.

Influence of mass on chemical action.—That the relative degrees of affinity of a body for a number of others to which it is simultaneously presented, are greatly modified by their relative masses, was first pointed out by Berthollet. The law laid down by that philosopher respecting the action of masses, is this:—*A body to which two different substances, capable of uniting with it chemically, are presented in different proportions, divides itself between them in the ratio of the products of their masses, and the absolute strengths of their affinities for the first*

body. Thus, if we denote by A and B the masses of the two bodies which are present in excess, by α and β, the coefficients of their absolute affinities for the body C; and by a and b, the quantities of A and B, which actually combine with C, the law just stated will be expressed by the proportion:—

$$a : b = \alpha A : \beta B.$$

If this view be correct, any alteration, however small, in the relative quantities of A and B, must produce a corresponding alteration in the relative quantities of the two which unite with C. That this is not the case under all circumstances, is shown by the following experiments of Bunsen and of Debus.

Bunsen's experiments,* which were made in such a manner that all the phenomena of combination concerned in them took place simultaneously, lead to the following remarkable laws:—

1. When two or more bodies, B B' . . . are presented in excess to the body A, under circumstances favourable to their combination with it, the body A always selects of the bodies B B' . . . quantities which stand to one another in a simple atomic relation, so that for 1, 2, 3 . . . atoms of the one compound, there are always formed 1, 2, 3 . . . atoms of the other; and if in this manner there is formed an atom of the compound AB', in conjunction with an atom of AB, the mass of the body B may be increased relatively to that of B', up to a certain limit, without producing any alteration in the atomic proportion.

When carbonic oxide and hydrogen are exploded with a quantity of oxygen not sufficient to burn them completely, the oxygen divides itself between the two gases in such a manner that the quantities of carbonic acid and water produced stand to one another in a simple atomic proportion. The results of Bunsen's experiments are given in the following table, the numbers in which denote volumes:—

* Ann. Ch. Pharm. lxxxv. 137.

Composition of Gaseous Mixture.			Quantities of CO and H consumed by Detonation.		Ratio of CO : H.
72·57 CO	18·29 H	9·14 O	12·18 CO	6·10 H	2 : 1
59·93 „	26·71 „	13·36 „	13·06 „	13·66 „	1 : 1
36·70 „	42·17 „	21·13 „	10·79 „	31·47 „	1 : 3
40·12 „	47·15 „	12·73 „	4·97 „	20·49 „	1 : 4

The results were the same whether the explosion took place in the dark, in diffused daylight, or in sunshine; and were not affected by the pressure to which the gaseous mixture was subjected.

The proportions of hydrogen and carbonic acid consumed in these several experiments, correspond with the composition of five hydrates of carbonic acid, containing, respectively—

$$HO.2CO_2;\ HO.CO_2;\ 2HO.CO_2;\ 3HO.CO_2;\ 4HO.CO_2;$$

but the results cannot be attributed to the actual formation of these hydrates, inasmuch as hydrates of acids containing several atoms of water are incapable of existing at high temperatures.

2. When a body, A, exerts a reducing action on a compound, BC, present in excess, so that A and B combine together, and C is set free; then, if C can, in its turn, exert a reducing action on the newly-formed compound, AB, the final result of the action is, that the reduced portion of BC is to the unreduced portion in a simple atomic proportion.

In this case, also, the mass of the one constituent may, without altering the existing atomic relation, be increased to a certain limit, above which that relation undergoes changes by definite steps, but always in the proportion of simple rational numbers.

When vapour of water is passed over red-hot charcoal, the carbon is oxidised and hydrogen is separated; but the process does not go on so far as the complete formation of carbonic acid, but stops at the point at which 1 vol. carbonic acid and 2 vol. carbonic oxide are formed to every 4 vol. of hydrogen.

In the imperfect combustion of cyanogen—the gaseous mixture being so far diluted that it will but just explode, in order that the temperature may not rise too high, and the result be consequently vitiated by the partial oxidation of the nitrogen—carbonic acid and carbonic oxide are formed, and nitrogen set free, likewise in simple atomic proportion. A mixture of 18·05 vol. cyanogen, 28·87 oxygen, and 53·08 nitrogen, gave, by detonation, 2 vol. carbonic oxide, and 4 vol. carbonic acid to 3 vol. nitrogen.

In the combustion of a mixture of carbonic acid, hydrogen, and oxygen, in which the carbonic acid is exposed at the same time to the reducing action of the hydrogen and the oxidising action of the oxygen, the reduced portion of the carbonic acid is likewise found to bear to the unreduced portion a simple atomic relation. In the combustion of a mixture of 8·52 carbonic acid, 70·33 hydrogen, and 21·15 oxygen, the resulting carbonic oxide was to the reduced carbonic acid in the ratio of 3 : 2. After the combustion of a mixture of 4·41 vol. carbonic oxide, 2·96 carbonic acid, 68·37 hydrogen, and 24·26 oxygen, the volume of the carbonic oxide converted into carbonic acid by oxidation, was to that of the residual carbonic oxide as 1 : 3.

That these remarkable laws had not been previously observed is attributed by Bunsen to the fact that they held good only when the phenomena of combination, which are regulated by them, take place simultaneously; for, even if a body *A*, were originally to select for combination from the bodies *B* and *C*, quantities bearing to one another a simple atomic relation, but the combination of *A* and *B* were to take place in a shorter time than that of *A* and *C*, it would follow of necessity, that during the whole of the process, the ratio of *B* to *C*, and therefore, also the atomic relations of the associated compounds, would change, so that the observed proportion would be no longer definite. The same result must follow if the bodies which are combining side by side are not homogeneously mixed in the beginning.

With regard to the bearing of these results on Berthollet's law, it might be objected that, in some of the experiments, as in the combustion of a mixture of carbonic oxide, hydrogen, and oxygen, one of the products, viz. the water, is removed from the sphere of action by condensation, and that the circumstances are therefore similar to the removal of an insoluble product by precipitation (I. 231). It is scarcely conceivable, however, that a reverse action would take place, even if the gaseous mixture were to remain at the temperature which exists during the combustion. Moreover, in the decomposition of vapour of water by red-hot charcoal, the whole of the products remain in the gaseous state.

Debus* has obtained results similar to those of Bunsen by precipitating mixtures of lime and baryta-water with aqueous carbonic acid, or mixtures of chloride of barium and chloride of calcium, with carbonate of soda. A small quantity of a very dilute solution of carbonate of soda, added to a liquid containing 5 pts. of chloride of barium to 1 pt. of chloride of calcium, threw down nearly pure carbonate of lime; but when the proportion of the chloride of barium in the mixture was 5·7 times as great as that of the chloride of calcium, 2·3 pts. of the former were decomposed to 1 pt. of the latter. Hence it appears that, in this reaction also, limits exist at which the ratio of the affinities undergoes a sudden change. In these experiments, however, the products are immediately removed from the sphere of action, and the results are therefore not comparable with those which are obtained when all the substances present remain mixed and free to act upon each other.

The latter condition is most completely fulfilled in the mutual actions of liquid compounds, such as solutions of salts, when all the possible products of their mutual actions are likewise soluble; as, for example, when nitrate of soda in solution is mixed with sulphate of copper. The question to be solved in such cases is this. Suppose two salts AB, CD,

* Ann. Ch. Pharm. lxxxv. 103.; lxxxvi. 156.; lxxxvii. 238.

the elements of which can form only soluble products by their mutual interchange, to be mixed together in solution. Will these elements, according to their relative affinities, either remain in their original state of combination, as AB and CD, or pass completely into the new arrangement AD and CB?—or will each of the two acids divide itself between each of the two bases, producing the four compounds AB, AD, BC, BD?—and, if so, in what manner will the relative quantities of these four compounds be affected by the original quantities of the two salts? Do the amounts of AD and CB, produced by the reaction, increase progressively with the regular increase of AB, as required by Berthollet's theory? or do sudden transitions occur, like those observed in the experiments of Bunsen and Debus?

The solution of this question is attended with considerable difficulty. For when two salts in solution are mixed, and nothing separates out, it is by no means easy to ascertain what changes may have taken place in the liquid. The ordinary methods of ascertaining the composition of the mixture, such as concentration, or precipitation by re-agents, are inadmissible, because any such treatment immediately alters the mutual relation of the substances present. In some cases, however, the mixture of two salts is attended with a decided change of colour, without any separation of either of the constituents, and such alterations of colour may afford indications of the changes which take place in the arrangement of the molecules. This method has been employed by Dr. Gladstone *, who has carefully examined the changes of colour attending the mixture of a great variety of salts, and applied the results to the determination of the effect of mass in influencing chemical action.

Dr. Gladstone's principal experiments were made with the blood-red sulphocyanide of iron, which is formed on adding hydro-sulphocyanic acid or any soluble sulphocyanide to a solution of a ferric salt (I. 532). On mixing known quantities

* Phil. Trans. 1855, 179; Chem. Soc. Qu. Jo. ix. 54.

of different ferric salts with known quantities of different sulphocyanides, it was found that the iron was never completely converted into the red salt; that the amount of it so converted depended on the nature both of the acid combined with the ferric oxide, and of the base combined with the sulphocyanogen; and that it mattered not how the bases and acids had been combined previous to their mixture, so long as the same quantities were brought together in solution. The effect of mass was tried by mixing equivalent proportions of ferric salts and sulphocyanides, and then adding known amounts of one or the other compound. It was found that, in either case, the amount of the red salt was increased, and in a regular progression according to the quantity added. When sulphocyanide of potassium was mixed in various proportions with ferric nitrate, chloride, or sulphate, the rate of variation appeared to be the same, but with hydrosulphocyanic acid it was different. The deepest colour was produced when ferric nitrate was mixed with sulphocyanide of potassium; but even on mixing 1 eq. of the former with 3 eq. of the latter, only 0·194 eq. of the red sulphocyanide of iron was formed; and even when 375 eq. of sulphocyanide of potassium had been added, there was still a recognisable amount of ferric nitrate undecomposed. The results of a series of experiments with ferric nitrate and sulphocyanide of potassium are given in the following table:—

Ferric Nitrate.	Sulphocyanide of Potassium.	Red Salt produced.	Ferric Nitrate.	Sulphocyanide of Potassium.	Red Salt produced.
1 equiv.	3 equiv.	88	1 equiv.	63 equiv.	356
1 „	6 „	127	1 „	99 „	419
1 „	9·6 „	156	1 „	135 „	487
1 „	12·6 „	176	1 „	189 „	508
1 „	16·2 „	195	1 „	243 „	539
1 „	19·2 „	213	1 „	297 „	560
1 „	28·2 „	266	1 „	375 „	587
1 „	46·2 „	318			

The addition of a colourless salt reduced the colour of a solution of ferric sulphocyanide, the reduction increasing in a regularly progressive ratio, according to the mass of the colourless salt.

Similar results were obtained with other ferric salts, viz., with the black gallate, the red meconate and pyromeconate, the blue solution of Prussian blue in oxalic acid, &c., and likewise with the coloured salts of other metals, *e. g.* the scarlet bromide of gold, the red iodide of platinum, the blue sulphate of copper, when treated with different chlorides, &c.

The amount of fluorescence exhibited by a solution of acid sulphate of quinine was found to be affected by the mixture of a chloride, bromide, or iodide, according to the nature and mass of the salt added; and the addition of sulphuric, phosphoric, nitric, and other acids was found to produce a fluorescence in solutions of hydrochlorate of quinine or of sulphate which had been rendered non-fluorescent by the addition of hydrochloric acid. Solutions of horse-chestnut bark, and of tincture of thorn-apple, yielded similar results.

The conclusions to be drawn from Dr. Gladstone's experiments, which afford a complete confirmation of Berthollet's theory, so far at least as relates to the action of substances in solution, are as follows: —

When two or more binary compounds are mixed under such circumstances that all the resulting compounds are free to act and react, each electro-positive element enters into combination with each electro-negative element in certain constant proportions, which are independent of the manner in which the different elements are primarily arranged, and are not merely the resultant of the various strengths of affinity of the several substances for each other, but are dependent also on the mass of each of the substances present in the mixture. All deductions respecting the arrangement of substances in solution, drawn from such empirical rules as that the strongest acid combines with the strongest base, must therefore be fallacious.

An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio, sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

This equilibrium of affinities arranges itself in most cases in an inappreciably short time; but, in certain instances, the elements do not attain their final state of combination for hours.

Totally different phenomena present themselves where precipitation, volatilisation, crystallisation, and perhaps other actions occur, simply because one of the substances is thus removed from the field of action, and the equilibrium, which was at first established, is thus destroyed (I. 231).

The reciprocal action of salts in solution has also been examined by Malaguti*, whose method consists in taking two salts, both of which are soluble in water, but only one of which is soluble in alcohol, mixing them in equivalent proportions in water, then pouring the aqueous solution into a large quantity of alcohol, and analysing the precipitate, in order to ascertain the quantities of the original salts which have been decomposed. Malaguti concludes from his experiments that, in the mutual action of two salts, if nothing separates from the liquid, the decomposition is most complete when the strongest acid and the strongest base are not originally united in the same salt, and that two experiments of this kind, made in opposite ways, must lead to the same final result; that, for example, when 1 eq. of acetate of baryta is added to 1 eq. of nitrate of lead, the quantities of nitrate of baryta and nitrate of lead ultimately present in the liquid are the same as when 1 eq. nitrate of baryta is mixed with 1 eq. acetate of lead. The greater the quantity of the two salts decomposed in the one case, the smaller will be the quantity

* Ann. Ch. Phys. [3], xxxvii. 198.

decomposed in the other; so that if the quantity of any salt, out of 100 parts, which is decomposed by the action of another salt (always supposing that the whole remains in solution) be called the *coefficient of decomposition*, the law of the reaction is, that the sum of the coefficients of decomposition in the two cases is always equal to 100. For example: if 1 at. sulphate of potash and 1 at. acetate of soda act upon each other, and $\frac{64}{100}$ of the original quantity of sulphate of potash remain in solution as such, the coefficient of decomposition is 36. The numerical values of the coefficients of decomposition, determined in several cases by the method above described, are given in the following table: —

Salts.	Coefficient of Decom-position.	Salts.	Coefficient of Decom-position.
Acetate of potash . . } Nitrate of lead . . . }	92·0	Acetate of lead . . . } Nitrate of potash . . }	9 0
Chloride of potassium . } Sulphate of zinc . . . }	84·0	Chloride of zinc . . . } Sulphate of potash . . }	17·6
Acetate of baryta . . } Nitrate of lead . . . }	77·0	Acetate of lead . . . } Nitrate of baryta . . }	22·0
Chloride of sodium . . } Sulphate of zinc . . . }	72·0	Chloride of zinc . . . } Sulphate of soda . . }	29·0
Acetate of baryta . . } Nitrate of potash . . }	72·0	Acetate of potash . . } Nitrate of baryta . . }	27·0
Acetate of potash . . } Nitrate of strontia . . }	67·0	Acetate of strontia . . } Nitrate of potash . . }	36·0
Acetate of strontia . . } Nitrate of lead . . . }	65·5	Acetate of lead . . . } Nitrate of strontia . . }	33·0
Acetate of potash . . } Sulphate of soda . . }	62·0	Acetate of soda . . . } Nitrate of potash . . }	36·5
Chloride of potassium . } Manganous sulphate . }	58·0	Manganous chloride . } Sulphate of potash . . }	42·5
Chloride of potassium . } Sulphate of magnesia . }	56·0	Chloride of magnesium } Sulphate of potash . . }	43·0
Chloride of sodium . } Sulphate of magnesia . }	54·5	Chloride of magnesium } Sulphate of soda . . }	45·8

In all these cases, except one, the coefficients of decomposition are greatest when the strongest acid and the strongest base are not originally united in the same salt. The exceptional case is presented by the mixture of nitric acid,

acetic acid, potash, and baryta, in which the greatest coefficient of decomposition is obtained when the nitric acid is at first united, not with the baryta, but with the potash. A similar result was obtained by the action of potash on nitrate of baryta and of baryta on nitrate of potash, wood-spirit being used as the precipitating agent instead of alcohol. The coefficient of decomposition was 6·9 in the former case, and 93·6 in the latter.

It is not easy to determine how far the particular numerical results of these experiments were influenced by the presence of the alcohol; but as its action was the same in both cases of each pair of experiments, the results certainly justify the conclusion that the two salts, when mixed, resolve themselves into four; that the partition takes place in a definite manner; and that the proportions of the resulting salts are independent of the manner in which their elements were originally combined.

Experiments bearing on the same point, have also been published by Margueritte*, who finds that two salts in solution mutually decompose each other, even when one of them is already the least soluble of the four salts that may be produced from the two acids and the two bases present. A saturated solution of chlorate of potash, to which chloride of sodium is added, becomes capable of dissolving an additional quantity of chlorate of potash, showing that a portion of the chlorate has been decomposed, and a more soluble salt formed. Chloride of ammonium is precipitated from its saturated aqueous solution on addition of a small quantity of nitrate of ammonia; but the previous addition of chlorate of potash prevents the precipitation; whence it would appear that the chlorate of potash and chloride of ammonium are partially converted into chlorate of ammonia and chloride of potassium. The precipitation of sulphate of lime from its aqueous solution by alcohol, is prevented by the presence of the nitrates

* Compt. rend. xxxviii. 304.

or chlorides of potassium, sodium, or ammonium, evidently because a portion of the sulphate is converted into nitrate or chloride. A solution of chloride of ammonium dissolves the carbonates of baryta, strontia, and lime more readily than pure water, because it partially converts them into chlorides, the liquid at the same time acquiring an alkaline reaction, in consequence of the formation of carbonate of ammonia.

The decomposition of insoluble by soluble salts affords a striking instance of the tendency of atoms to interchange, and of the influence of mass on chemical action. According to H. Rose*, sulphate of baryta is completely decomposed by boiling with solutions of alkaline carbonates, provided that each equivalent of sulphate of baryta is acted upon by at least 15 eq. of the alkaline carbonate. If 1 eq. of sulphate of baryta is boiled with only 1 eq. of carbonate of potash, only $\frac{1}{9}$ of it is decomposed, and only $\frac{1}{11}$ by boiling with 1 eq. of carbonate of soda, further decomposition being prevented by the presence of the alkaline sulphate already formed. If, however, the liquid be decanted after a while, the residue boiled with a fresh portion of the alkaline carbonate, and these operations repeated several times, complete decomposition is effected. Carbonate of baryta is converted into sulphate by the action of an aqueous solution of sulphate of potash or soda, even at ordinary temperatures. Solution of carbonate of ammonia does not decompose sulphate of baryta either at ordinary or at higher temperatures; carbonate of baryta is not decomposed by sulphate of ammonia at ordinary temperatures, but easily on boiling. Sulphate of baryta is not decomposed by boiling with caustic potash-solution, provided the carbonic acid of the air be excluded; but by fusion with hydrate of potash, it is decomposed, with formation of carbonate of baryta, because the carbonic acid of the air cannot then be completely excluded. Hydrochloric and

* Pogg. Ann. xciv. 481; xcv. 96, 284.

nitric acids, left in contact at ordinary temperatures with sulphate of baryta, either crystallised or precipitated, dissolve only traces of it; at the boiling heat, a somewhat larger quantity is dissolved, and the solution forms a cloud, both with a dilute solution of chloride of barium and with dilute sulphuric acid. Sulphate of strontia is dissolved by hydrochloric acid at ordinary temperatures, sufficiently to form a slight precipitate with dilute sulphuric acid, and with chloride of strontium. Sulphate of lime treated with hydrochloric acid, either cold or boiling, yields a liquid in which a precipitate is formed, after a while, by dilute sulphuric acid, but not by chloride of calcium.

Sulphate of strontia and sulphate of lime are completely decomposed by solutions of the alkaline carbonates and bicarbonates at ordinary temperatures, and more quickly on boiling, even if considerable quantities of an alkaline sulphate are added to the solution: the decomposition is also effected by carbonate of ammonia, even at ordinary temperatures. The carbonates of strontia and lime are not decomposed by solutions of the sulphates of potash or soda at any temperature; sulphate of ammonia does not decompose them at ordinary temperatures, but readily with the aid of heat.

Sulphate of lead is completely converted into carbonate by solutions of the alkaline carbonates and bicarbonates, even at ordinary temperatures, the neutral carbonates, but not the bicarbonates, then dissolving small quantities of oxide of lead. Carbonate of lead is not decomposed by solutions of the alkaline sulphates, either at ordinary temperatures or on boiling.

Chromate of baryta is decomposed at ordinary temperatures by solutions of the neutral alkaline carbonates, and much more easily by boiling with excess of an alkaline bicarbonate. When equivalent quantities of the chromate of baryta and carbonate of soda are boiled with water, $\frac{1}{7}$ of the whole is decomposed; when the same quantities of the salts

are fused together, and the mass treated with water, only $\frac{1}{21}$ of the baryta-salt is decomposed. Carbonate of baryta is completely converted into chromate by digestion with a solution of an alkaline monochromate; and the decomposition of chromate of baryta by alkaline carbonates, even at the boiling heat, is completely prevented by the presence of a certain quantity of an alkaline monochromate.

Seleniate of baryta is easily and completely decomposed by solutions of alkaline carbonates, even at ordinary temperatures: this salt is somewhat soluble in water, and more readily in dilute acids.

Oxalate of lime is decomposed by alkaline carbonates even at ordinary temperatures; but to effect complete decomposition the liquid must be frequently decanted and renewed. The decomposition takes place rapidly at the boiling heat; but in all cases it is completely prevented by the presence of a certain quantity of a neutral alkaline oxalate. When the salts are mixed in equivalent proportions, $\frac{2}{17}$ of the oxalate of lime are decomposed at ordinary temperatures, and $\frac{5}{8}$ on boiling. Carbonate of lime is partially converted into oxalate by the action of a solution of neutral oxalate of potash at ordinary temperatures, and more quickly on boiling;—but the decomposition is never complete, even when the liquid is frequently decanted and renewed.—Oxalate of lead is completely converted into carbonate at ordinary temperatures by the solution of an alkaline carbonate, a small portion of the carbonate of lead dissolving in the liquid. (Rose.)

The preceding experiments exhibit in a striking manner the influence of difference of solubility in determining the order of decomposition. Sulphate of baryta is less soluble than the carbonate, and, accordingly, carbonate of baryta is more readily decomposed by alkaline sulphates, than the sulphate by alkaline carbonates. Precisely the contrary relations are exhibited by the sulphates and carbonates of

strontia* and lime, both as regards solubility and order of decomposition. On the other hand, oxalate of lime is less soluble than the carbonate, and yet its decomposition by alkaline carbonates takes place more easily than the opposite reaction: in this case, the order of decomposition appears rather to be determined, as in Malaguti's experiments, by the tendency of the strongest acid to unite with the strongest base.

The effect of a soluble sulphate, &c., in arresting the decomposition of the corresponding insoluble salts by alkaline carbonates, is evidently due to its tendency to produce the reverse action: hence the acceleration produced by decanting and renewing the liquid. Some insoluble salts, however, phosphate of lime for example, are never completely decomposed, even by this treatment.

The constant tendency to interchange of atoms, exhibited in the phenomena above described, and, indeed, in all cases of chemical action, suggests the idea that the atoms of all bodies, at least in the fluid state, are in constant motion. We have already seen that the same idea is suggested by the phenomena of heat, and leads to a consistent theory of those phenomena (II. 449). On a similar hypothesis, Professor Williamson proposes to construct a general theory of chemical action.† The fundamental notion of this theory is, that the atoms of all compounds, whether similar or dissimilar, are continually changing places, the interchange taking place more readily as the atoms resemble each other more closely. Thus, in a mass of hydrochloric acid, each atom of hydrogen is supposed, not to remain quietly in juxta-position with the atom of chlorine with which it happens to be first united, but to be continually changing places with other atoms of hydrogen, or, what comes to the same thing, continually becoming associated with other atoms of chlorine. This interchange is

* According to Fresenius, carbonate of strontia dissolves in 11,862 parts, and the sulphate in 6895 parts of cold water.

† Chem. Soc. Qu. J., iv. 110.

not perceptible to the eye, because one molecule of hydrochloric acid is exactly like another. But suppose the hydrochloric acid to be mixed with a solution of sulphate of copper (the component atoms of which are likewise undergoing a change of place), the basylous elements, hydrogen and copper, then no longer limit their change of place to the circle of atoms with which they were at first combined, but the hydrogen and copper likewise change places with each other, forming chloride of copper and sulphuric acid. Thus it is that, when two salts are mixed in solution, and nothing separates out in consequence of their mutual action, the bases are divided between the acids, and four salts are produced. If, however, the analogous elements of the two compounds are very dissimilar, and, consequently, interchange but slowly, it may happen that the stronger acid and the stronger base remain almost entirely together, leaving the weaker ones combined with each other. This is strikingly seen in a mixture of sulphuric acid (sulphate of hydrogen) and borate of soda, which soon becomes almost wholly converted into sulphate of soda and free boracic acid (borate of hydrogen).

Now suppose that, instead of sulphate of copper, sulphate of silver is added to the hydrochloric acid. At the first moment the interchange of elements may be supposed to take place as above, and the four compounds, SO_4H_2, SO_4Ag_2, ClH, and $ClAg$, to be formed; but the last, being insoluble, is immediately removed by precipitation; the remaining elements then act upon each other in the same way, and this action goes on till all the chlorine or all the silver is removed in the form of chloride of silver; if the original compounds are mixed in exactly equivalent proportions, the final result is the formation of only two salts, viz., in this case, SO_4H_2 and $ClAg$. A similar result is produced when one of the products of the decomposition is volatile at the existing temperature, as when hydrate or carbonate of soda is boiled with chloride of ammonium.

This theory affords a simple explanation of the action of sulphuric acid upon alcohol, whereby sulphovinic acid (sulphate of ethyl and hydrogen) is first formed, and afterwards, at a certain temperature, ether and water are eliminated (I. 226). When alcohol, $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$, and sulphuric acid, $\left.\begin{matrix}H\\H\end{matrix}\right\}SO_4$, are mixed together, the interchange between the atoms of ethyl in the former and of hydrogen in the latter gives rise to the formation of sulphovinic acid and water:—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4 = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}H\\H\end{matrix}\right\}O.$$

But the change does not stop here, for the sulphovinic acid thus produced, meeting with fresh molecules of alcohol, exchanges its ethyl for the hydrogen of the alcohol, producing ether and sulphuric acid:—

$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4.$$

The sulphuric acid is thus restored to its original state, and is ready to act upon fresh quantities of alcohol; so that if alcohol be allowed to run into the mixture in a constant stream, the temperature being kept within certain limits (between 140° and 160° C.), the process goes on without interruption, ether and water continually distil over, and the same quantity of sulphuric acid suffices for the etherification of an unlimited quantity of alcohol. This is the peculiarity of the process; it has given rise to a variety of explanations; in fact, the process of etherification has long been a battle-ground of chemical theories.* The discussion of these various theories would be foreign to the present purpose; it is sufficient to remark that the hypothesis of atomic interchange affords a ready explanation of the most obscure point in the

* See the translation of Gmelin's Handbook, vol. viii. pp. 231—237.

reaction, viz., the formation and decomposition of sulphovinic acid following each other continuously, without any change of temperature or other determining cause. If it be admitted that the atoms of ethyl and hydrogen in the mixture are continually interchanging in all possible ways, this series of alternate actions follows as a necessary consequence.

The formation of ether by the mutual action of sulphovinic acid and alcohol is also analogous to its production by the action of iodide of ethyl on potassium-alcohol (p. 534):—

$$\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O + C_2H_5I = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + KI.$$

The same view is corroborated by the fact recorded by Williamson, in the paper above quoted, that sulphamylic acid (sulphate of amyl and hydrogen) distilled with common alcohol, yields an ether containing both ethyl and amyl:—

$$\left.\begin{matrix}C_5H_{11}\\H\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO_4;$$

and that the same compound is obtained by distilling a mixture of vinic and amylic alcohols with sulphuric acid; also with the fact discovered by Chancel, that sulphovinate of potassium distilled with potassium-alcohol, yields ether:—

$$\left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}K\\K\end{matrix}\right\}SO_4;$$

and that the same salt distilled with methylate of potassium, CH_3KO, yields methamylic ether, $\left.\begin{matrix}C_2H_5\\CH_3\end{matrix}\right\}O$.

The idea of atomic motion is in accordance with physical as well as chemical phenomena. To suppose that rest, rather than motion, is the normal state of the particles of matter, is at variance with all that we know of the effects of light, heat, and electricity. In the heat-theory of Clausius, (II. 449), the particles of bodies are supposed to be affected

with progressive, as well as with rotatory and vibratory movements; and this same hypothesis of progressive movement which, of course, implies change of relative position among the particles, affords, as already stated, a ready explanation of certain chemical reactions, otherwise somewhat obscure. It is worth while to observe that, in the heat-theory of Clausius, the progressive motion of the particles is supposed to exist only in the liquid and gaseous states, the particles of solid bodies merely performing rotatory and vibratory movements about certain positions of equilibrium. This is quite in accordance with the well-known fact that chemical reaction rarely takes place between solid bodies.

DIFFUSION OF LIQUIDS.

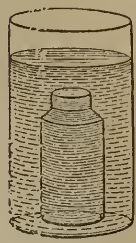
Intimately connected with the interchange of atoms resulting in chemical decomposition, is the process by which a saline, or other soluble substance, is spread or diffused uniformly through the mass of the solvent; in some cases, indeed, as will presently be seen, the decomposition of salts is greatly facilitated by the tendency of one or more of the products of decomposition to diffuse into the surrounding liquid.

The phenomena of liquid diffusion have been minutely investigated by Mr. Graham.* The apparatus used consisted of a set of phials, of nearly equal capacity, cast in the same mould, and further adjusted by grinding to a uniform size of aperture. The phials were 3·8 inches high, with a neck 0·5 inch in depth, and aperture 1·25 inch wide; capacity to base of neck equal to 2080 grains of water, or between 4 and 5 ounces. For each *diffusion-phial*, a plain glass *water-*

* Phil. Trans. 1850, pp. 1, 805; Chem. Soc. Qu. J. ii. 60, 257; iv. 83.

jar was also provided, 4 inches in diameter and 7 inches deep. (Fig. 43).

Fig. 43.



The diffusion-phial was filled with the saline solution, sal-ammoniac for instance, to the base of the neck, or more correctly to a distance of 0·5 inch from the ground surface of the lip. The neck of the phial was then filled up with distilled water, a light float being first placed on the surface of the solution, and care being taken to avoid agitation. After the phial had been placed within the jar, water was poured into the jar, so as to cover the open phial to the depth of an inch, which required about 20 ounces of water. The saline liquid in the phial is thus allowed to communicate freely with the water in the jar. The diffusion is interrupted by placing a small plate of ground glass on the mouth of the phial, and raising the latter out of the jar. The amount of salt diffused, called the *diffusion-product*, or *diffusate*, is ascertained by evaporating the water in the jar to dryness, or, in the case of chlorides, by precipitating with nitrate of silver.

The results of several series of experiments made in this manner are given in the following Table, the second column of which shows the quantity of salt in 100 parts of the solution; the third, the time of diffusion; the fourth, the temperature, on the Fahrenheit scale; the fifth, the quantity of salt diffused:—

DIFFUSION OF SALINE SOLUTIONS.

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Hydrochloric acid	1	5	51°	7·41
	2	5	51	15·04
	2	5	59·7	16·55
	4	5	51	30·72
	8	5	51	67·68
Hydriodic acid	2	5	51	15·11
Hydrobromic acid	2	5	59·7	16·58
Bromine	0·864	10	60·1	5·84
Hydrocyanic acid	1·766	5	64·2	11·68
Hydrated nitric acid (NO_6H)	1	5	51·2	6·99
	2	5	51·2	14·74
	4	5	51·2	28·76
	8	5	51·2	57·92
Hydrated sulphuric acid (SO_4H)	1	10	49·7	8·69
	2	10	49·7	16·91
	4	10	49·7	33·89
	8	10	49·7	68·96
Chromic acid	1·762	10	67·3	19·78
Acetic acid ($C_4H_4O_4$)	2	10	48·8	11·31
	4	10	48·8	22·02
	8	10	48·8	41·80
Sulphurous acid	1	10	68·1	8·09
	2	10	68·1	16·96
	4	10	68·1	33·00
	8	10	68·1	66·38
Ammonia	1	4·04	63·4	4·93
	2	4·04	63·4	9·59
	4	4·04	63·4	19·72
	8	4·04	63·4	41·22
Alcohol	2	10	48·7	8·62
	4	10	48·7	16·12
	8	10	48·7	35·50
Nitrate of baryta	1	11·43	64·1	7·72
	2	11·43	64·1	15·04
	4	11·43	64·1	29·60
	8	11·43	64·1	54·50
Nitrate of strontia	0·82	11·43	51·5	5·59
Nitrate of lime	1	11·43	64·1	7·66
	2	11·43	64·1	15·01
	4	11·43	64·1	29·04
	8	11·43	64·1	55·10
Acetate of baryta	1	16·17	53·5	7·50
Acetate of lead	1	16·17	53·1	7·84
Chloride of barium	1	8·57	6·3	6·32
	2	8·57	6·3	12·07
	4	8·57	6·3	23·96
	8	8·57	6·3	45·92
Chloride of strontium	1	8·57	6·3	6·09
	2	8·57	6·3	11·66
	4	8·57	6·3	23·56
	8	8·57	6·3	44·46

DIFFUSION OF SALINE SOLUTIONS — *continued.*

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Chloride of calcium . .	1	11·43	63·8°	7·92
	2	11·43	63·8	15·35
	4	11·43	63·8	30·78
	8	11·43	63·8	61·56
	1	11·43	50·8	6·51
Chloride of manganese . .	1	11·43	50·8	6·63
Nitrate of magnesia . .	1	11·43	50·8	6·49
Nitrate of copper . . .	1	11·43	50·8	6·44
Chloride of zinc . . .	1	11·43	50·8	6·29
Chloride of magnesium . .	1	11·43	50·8	6·17
Cupric chloride . . .	1	11·43	50·8	6·06
Ferrous chloride . . .	1	11·43	53·5	6·30
Sulphate of magnesia . .	1	16·17	65·4	7·31
	2	16·17	65·4	12·79
	4	16·17	65·4	23·46
	8	16·17	65·4	42·82
	8	16·17	62·8	42·66
	16	16·17	62·8	75·06
	24	16·17	62·8	102·04
Sulphate of zinc . . .	1	16·17	65·4	6·67
	2	16·17	65·4	12·22
	4	16·17	65·4	23·12
	8	16·17	65·4	42·26
	8	16·17	62·8	39·62
	16	16·17	62·8	74·40
	24	16·17	62·8	101·42
Sulphate of alumina . .	1	16·17	65·4	5·48
	2	16·17	65·4	10·21
	4	16·17	65·4	19·28
	8	16·17	65·4	33·52
Nitrate of silver . . .	2	7	63·4	13·61
	4	7	63·4	26·34
	8	7	63·4	51·88
Nitrate of soda . . .	2	7	63·4	12·35
	4	7	63·4	23·56
	8	7	63·4	47·74
Chloride of sodium . . .	1	7	63·4	6·32
	2	7	63·4	12·37
	4	7	63·4	24·96
	8	7	63·4	48·44
	2	7	63·4	12·14
Iodide of sodium . . .	2	7	59·8	12·18
Bromide of sodium . . .	2	7	59·8	12·14
Chloride of potassium . .	2	5·716	59·8	12·24
Bromide of potassium . .	2	5·716	59·8	12·46
Iodide of potassium . .	2	5·716	59·8	12·51
Chloride of ammonium . .	1	5·716	59·8	5·99
Bicarbonate of potash . .	1	8·08	68·2	7·23
	2	8·08	68·2	14·05
	4	8·08	68·2	26·72
	8	8·08	68·2	52·01
Bicarbonate of ammonia . .	1	8·08	68·2	6·91
	2	8·08	68·2	13·65

DIFFUSION OF SALINE SOLUTIONS — *continued.*

Substance.	Per Cent.	Days.	Fahr.	Diffusate.
Bicarbonate of ammonia	4	8·08	68·2°	27·00
	8	8·08	68·2	50·10
Bicarbonate of soda	1	9·87	68·2	7·31
	2	9·87	68·2	13·81
	4	9·87	68·2	26·70
	8	9·87	68·2	52·38
Hydrate of potash	1	4·04	63·3	6·56
	2	4·04	63·3	12·84
	4	4·04	63·3	25·04
	8	4·04	63·3	52·24
Hydrate of soda	1	4·95	63·2	5·81
	2	4·95	63·2	11·09
	4	4·95	63·2	20·86
	8	4·95	63·2	40·44
Carbonate of potash	1	8·08	63·6	6·13
	2	8·08	63·6	11·92
	4	8·08	63·6	22·88
	8	8·08	63·6	45·44
Carbonate of soda	1	9·9	63·4	6·02
	2	9·9	63·4	11·70
	4	9·9	63·4	21·42
	8	9·9	63·4	39·74
Sulphate of potash	1	8·08	60·2	6·16
	2	8·08	60·2	11·60
	4	8·08	60·2	22·70
	8	8·08	60·2	43·92
Sulphate of soda	1	9·9	59·9	6·33
	2	9·9	59·9	12·00
	4	9·9	59·9	21·96
	8	9·9	59·9	41·38
Sulphite of potash	2	8·08	59·5	11·63
Sulphite of soda	2	9·9	59·5	11·83
Hyposulphite of potash	2	8·08	59·7	12·37
Hyposulphite of soda	2	9·9	59·9	11·89
Sulphovinate of potash	2	8·08	59·7	12·60
Sulphovinate of soda	2	9·9	59·5	13·03
Oxalate of potash	1	8·08	59·9	6·20
	2	8·08	59·9	12·17
	4	8·08	59·9	23·04
	8	8·08	59·9	42·82
Oxalate of soda	1	9·9	59·9	6·24
Acetate of potash	1	8·08	60·2	6·44
	2	8·08	60·2	12·52
	4	8·08	60·2	23·44
	8	8·08	60·2	47·26
Acetate of soda	1	9·9	59·5	6·67
	2	9·9	59·5	12·46
	4	9·9	59·5	25·04
	8	9·9	59·5	48·04
Tartrate of potash	2	8·08	59·9	10·96
Tartrate of soda	2	9·9	59·5	10·65
Hydrochlorate of morphine	2	11·43	64·1	11·60
Hydrochlorate of strychnine	2	11·43	64·1	11·49

These experiments, and a number of others made in a similar manner, lead to the following general conclusions: —

1. Different salts, in solutions of equal strength, diffuse unequally in equal times.

2. With each salt, the rate of diffusion increases with the temperature, and at any given temperature, is proportionate to the strength of the solution, at least when the quantity of salt dissolved does not exceed 4 or 5 per cent.

3. There exist classes of equidiffusive substances which coincide in many cases with the isomorphous groups, but are, on the whole, more comprehensive than the latter. Thus, the same rate of diffusion is exhibited by hydrochloric, hydrobromic, and hydriodic acid; by the chlorides, iodides, and bromides of the alkali-metals; by the nitrates of baryta, strontia, and lime; the sulphates of magnesia and zinc, &c. &c.

4. For several groups of salts it is found that the squares of the times of equal diffusion, from solutions of the same strength, stand to one another in a simple numerical relation. Thus, the diffusate from a solution of nitrate of potash, in 7 days, was equal to that obtained from an equally strong solution of carbonate of potash, in 9·9 days, numbers which are to one another as $1 : \sqrt{2}$. Similar results were obtained with 2 per cent. solutions of nitrate and sulphate of potash, equal diffusates of the two being obtained in 3·5 and 4·95 days, in 7 and 9·9 days, and in 10·5 and 14·85 days; also, with hydrate and nitrate of potash, and with nitrate and carbonate of soda. The times of equal diffusion of 1 per cent. solutions of chloride of ammonium and chloride of sodium, were to one another as $\sqrt{2} : \sqrt{3}$. Now, according to Mr. Graham's experiments (I. 87), the squares of the times of equal diffusion of gases are to one another in the ratio of their densities. Hence, by analogy, it may be inferred that the molecules of these several salts, as they exist in solution, possess densities which are to one another as the squares of the times of equal

diffusion. Thus, the *solution-densities* of sulphate, nitrate, and hydrate of potash, are to one another as the numbers 4, 2, and 1. These solution-densities appear to relate to a kind of molecules different from the chemical atoms, and the weights of which are either equal, or bear to one another a simple numerical relation.

The diffusion of a salt into the solution of another salt takes place with nearly the same velocity as into pure water; at least, when the solutions are dilute. Mr. Graham has shown that the diffusion of a 4 per cent. solution of carbonate of soda, is not sensibly affected by the presence of 4 per cent. of sulphate of soda in the liquid atmosphere; nor that of a 4 per cent. solution of nitrate of potash, by the same proportion of nitrate of ammonia. The presence of 4 per cent. of sulphate of soda reduced the diffusion of carbonate of soda by only $\frac{1}{8}$ of the whole. In stronger solutions the retardation would probably be greater. There is, indeed, reason to believe that the phenomena of liquid diffusion are exhibited in their simplest form only by weak solutions, the effect of concentration, like that of compression in gases, being to produce a departure from the normal character.

The rate of diffusion is, however, materially affected when the liquid atmosphere already contains a portion of the diffusing salt. The consideration of this case leads to the general question of the motion of particles of a dissolved substance in a solution of unequal concentration. The general law which regulates such movements appears to be this: — *The velocity with which a soluble salt diffuses from a stronger into a weaker solution, is proportional to the difference of concentration between two contiguous strata.* This law has not yet been experimentally demonstrated in a sufficient number of cases to establish it completely; but in the case of chloride of sodium, it has been shown to be true by the following experiments of Fick.*

* Phil. Mag. [4], x. 30.

A cylindrical glass tube, open at both ends, was cemented into a vessel completely filled with common salt, the cylindrical space filled up with water, and the whole immersed in a large jar containing water. The apparatus was then left to itself for several weeks, the water in the jar being from time to time taken out and renewed. Now, as the lowest stratum of liquid in the tube, being in contact with undissolved salt, must remain constantly saturated, while the uppermost layer, which is in contact with pure water, contains no salt at all, a certain normal state of diffusion will ultimately establish itself throughout the length of the tube, characterised by the condition, that each horizontal stratum will, in a given time, give up to the stratum immediately above it as much salt as it receives from the one below. When this state is attained, the densities of the successive strata decrease from below upwards in arithmetical progression. This law of decrease was verified experimentally by immersing in the liquid, at various depths, a glass bulb suspended from the arm of a balance, and counterpoised by weights in the opposite scale. This law of decrease, however, is true only with regard to cylindrical columns of liquid, or others, in which the horizontal section is of uniform magnitude. In other cases, the law of decrease of density may be calculated according to the form of the vertical section. In funnel-shaped tubes, Fick has shown that the results of calculation agree with those of experiment.

Now let K denote the quantity of salt which, in the normal state of diffusion, passes in a unit of time through a unit of horizontal section of a cylindrical tube whose height is equal to the unit of length: this quantity is called the *diffusion-coefficient;* also, let Q be the quantity of salt which, in the time t, flows from the mouth of the tube into the water-atmosphere; h, the height of the tube; s, its horizontal section; and d, the density of the liquid at the bottom; then

$$Q = K \,.\, d \,.\, \frac{s}{h}\, t.$$

Hence, with a tube of given dimensions, and a solution of known and constant density at the bottom, the *diffusion-coefficient* K, of any salt, may be calculated from the quantity Q, diffused out in a given time.

This method has been applied by Fick only in the case of chloride of sodium. It is, in fact, though simple in principle, somewhat inconvenient of application, on account of the long time—at least 14 days—which must elapse before the normal state is attained.

Another method of determining the diffusion-coefficient of a salt has been devised by Jolly, and applied in several cases by Beilstein.* The apparatus used consists of a glass tube (Fig. 44), about three inches long, bent round at the bottom, and cut off near the bend, so that the level of the orifice is not much more than a millimeter above the bottom of the bend at a.

FIG. 44.

The upper end of the tube is slightly drawn out, and closed with a stopper. This tube is filled with a solution of known concentration, and fixed upright within a jar of water, the orifice of the tube being 2 or 3 lines below the level of the water. The salt then immediately begins to diffuse into the water, and as the liquid near the orifice becomes diluted, it passes round the bend to the upper part of the tube, its place being supplied by more concentrated liquid from above. With this apparatus, Beilstein has obtained the following diffusion-coefficients (taking that of chloride of potassium for unity), for solutions containing 4 per cent. of salt, and at the temperature of 6° C. (10·2° F.).

Chloride of potassium	1	Sulphate of potash	0·6987
Nitrate of potash	0·9487	Carbonate of soda	0·5436
Chloride of sodium	0·8337	Sulphate of soda	0·5369
Bichromate of potash	0·7543	Sulphate of magnesia	0·3587
Carbonate of potash	0·7371	Sulphate of copper	0·3440

Beilstein infers from his experiments, that the rate of dif-

* Ann. Ch. Pharm. xcix. 165.

fusion is not exactly proportional to the difference of density of two contiguous strata, but increases in a somewhat greater ratio.

Simmler and Wilde* are of opinion that the want of agreement of Beilstein's results with this law arises from a defect in the method of experimenting. Beilstein's calculations, indeed, are based on the supposition that the strength of the solution in the tube (Fig. 44), though constantly decreasing, is uniform at any instant of time throughout the entire length; whereas, a little consideration will show that the density near the orifice must be less than that in the larger arm of the tube, and in this arm less than near the bottom of the bend, where the liquid must stagnate to a certain extent. From this source of error, Fick's mode of observation is free. Simmler and Wilde, however, propose other methods, easier of execution than Fick's, and not subject to the necessity of waiting till the normal state of diffusion is established. One of these methods is similar to that adopted by Mr. Graham, excepting that the vessel containing the solution is perfectly cylindrical, a condition which greatly simplifies the calculations; and, instead of being placed at the bottom of the water-jar, is supported on a stand, so as to bring its mouth within a line or two below the surface of the water; the salt, as it diffuses out, is thus made to flow over the sides of the vessel and fall to the bottom, leaving an atmosphere of pure water above. Another method, proposed by the same authors, is to place the saline solution in a vessel having the form of a triangular prism, and determine the variation of density at different depths below the surface by observation of the indices of refraction. The numerical results obtained by these methods have not yet been published.

Mixed salts may be more or less separated by their unequal diffusibility. A solution of 1 part of carbonate of potash and 1 part of carbonate of soda in 10 parts of water, yielded in

* Pogg. Ann. C. 217.

19 days at 60° F. a diffusate containing 63·6 parts of carbonate of potash to 36·4 parts of carbonate of soda; the diffusate obtained in 25 days contained the two salts in nearly the same proportion. Sea-water was also partially decomposed by diffusion, the diffusate containing a smaller proportion of magnesia-salts than the residue. The variation of composition in the water of the Dead Sea, at different times of the year, probably arises from the unequal rate of diffusion of the different salts contained in the strong saline liquid into the layer of fresh water brought down to it during the rainy season. (Graham.)

Diffusion is also capable of effecting the decomposition of chemical compounds. From a solution of bisulphate of potash, saturated at 20° C. (68° F.), there were diffused in 50 days, 31·8 parts of bisulphate of potash, and 12·8 parts of hydrated sulphuric acid. A solution of 8 parts of anhydrous alum in 100 parts of water yielded, in 8 days, at 17·9° C. (64·2° F.), a diffusate of 5·3 parts alum and 2·2 parts sulphate of potash. A solution of 1 part of sulphate of potash in 100 parts of lime-water, left to diffuse into lime-water for seven days, yielded as a mean result, a diffusate containing 22·67 parts of hydrate of potash, and 77·33 parts of sulphate of potash. A similar experiment with sulphate of soda, yielded a diffusate containing about 12 per cent. of hydrate of soda. The larger quantity of the alkaline hydrate obtained in the first instance, appears to be due to the superior diffusibility of the sulphate of potash, as it can scarcely be supposed that the affinity of potash for sulphuric acid is less than that of soda. The sulphates of potash and soda were also decomposed by carbonate of lime dissolved in carbonic acid water, when the liquid was allowed to diffuse into pure water. The chlorides of potassium and sodium were not sensibly decomposed by lime-water in this manner. When saturated solutions of lime-water and sulphate of lime were mixed in equal volumes, 1 per cent. of chloride of sodium dissolved in the

mixture, and the solution left to diffuse into pure water, scarcely a trace of hydrate of soda was obtained; but when the solution of sulphate of lime, with an addition of 2 per cent. of chloride of sodium, was kept at the boiling point for half an hour, and the solution mixed two or three days afterwards with an equal volume of lime-water, and diffused into pure water for $3\frac{1}{2}$ days, the diffusate in three cells was found to contain 0·234 grains hydrate of soda, and 0·371 sulphate of soda. It appears, then, that more than one condition of equilibrium is possible for mixed solutions of sulphate of lime and chloride of sodium. Cold solutions of these salts may be mixed without decomposition, or, without sensible formation of sulphate; but, on heating, this change is induced, and is permanent, sulphate of soda being formed, and continuing to exist in the cold solution; for it is the decomposition of that salt alone by hydrate of lime which appears to yield the diffused hydrate of soda. As the effects of time and temperature are often convertible, it is possible that the same decomposition might take place at ordinary temperatures after a considerable time. "If such be the case, we have an agency in the soil, by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates, for the sulphate of lime, generally present, will convert those chlorides into sulphates. The mode in which the soil of the earth is moistened by rain, is peculiarly favourable to separations by diffusion. The soluble salts of the soil may be supposed to be carried down together, to a certain depth, by the first portion of rain which falls, while they find afterwards an atmosphere of nearly pure water, in the moisture which falls last and occupies the surface-stratum of the soil. Diffusion of the salts upwards into the water, with its separations and decompositions, must necessarily ensue. The salts of potash and ammonia, which are most required for vegetation, possess the highest diffusibility, and will rise first. The pre-eminent

diffusibility of the alkaline hydrates may also be called into action in the soil by hydrate of lime, particularly as quicklime is applied for a top-dressing to grass lands." (Graham.*)

PASSAGE OF LIQUIDS THROUGH POROUS SEPTA. OSMOSE.

The force of liquid diffusibility still acts when the two liquids are separated by a porous sheet of animal membrane, or unglazed earthenware; for the pores of such a membrane are occupied by water, and an uninterrupted liquid communication exists between the water on the one side, and the saline solution on the other. Under these circumstances, a flow of liquid takes place, generally, though not always, from the water to the saline solution, so that the quantity of liquid diminishes on one side of the septum, while it increases on the other. This phenomenon was originally designated by the correlative terms, *Endosmose* and *Exosmose;* but it is better expressed by the shorter word *Osmose* (from *ὤσμος*, impulsion), which includes the two former.

This passage of liquids through porous septa, was first studied by Dutrochet, whose apparatus, called an *endosmometer*, consisted of a narrow glass tube, having a funnel-shaped expansion at the bottom, and closed at that end by a piece of bladder. This tube was filled with a saline solution, and placed in a vertical position, in a jar containing water. The flow of liquid in one direction or the other, was measured by the rise or fall of the liquid in the tube. Dutrochet inferred from his experiments that the velocity of the osmotic current is proportional to the quantity of salt or other solid substance originally contained in the saline solution. The experiments were, however, inexact, because no allowance was made for the alteration of hydrostatic pressure, caused by the rise or fall of liquid in the tube. Vierordt †, who used a modification of Dutrochet's apparatus, in which this source of error was

* Chem. Soc. Qu. J. iii. 67.

† Pogg. Ann. lxxiii. 519.

removed, found that the velocity of the current increases with the initial concentration of the solution, but in a lower ratio.

Professor Jolly of Heidelberg, has examined the osmose of water and saline solutions by a different method. The saline solution containing a known quantity of salt, is contained in a glass tube closed at the bottom with bladder, and plunged into water, which is frequently changed, so as to keep it nearly pure. The tube with its contents is taken out from time to time and weighed, and these operations are repeated till the weight becomes constant, showing that the whole of the salt has passed out from the tube, and nothing but water remains.

In this manner, it is found that a given quantity of any salt which passes through the septum into the water is always replaced by a definite quantity of water. The quantity of water which is thus replaced by a unit of weight of the salt, is called the *endosmotic* (or *osmotic*) *equivalent* of that salt. This quantity varies with the nature of the salt, and with the temperature, increasing as the temperature rises, but it is independent of the density of the solution. At temperatures near 0° C., the endosmotic equivalent of hydrate of potash was found to be 200; of chloride of sodium, between 4·3 and 4·6; of sulphate of soda, between 11 and 12; of neutral sulphate of potash, 12; of acid sulphate of potash, 2·3; and of hydrated sulphuric acid (at 18° C.), 0·35.

These results point to the conclusion, that the osmose between water and saline solutions, consists, not in the opposite passage of two liquid currents, but in the passage of particles of the salt in one direction, and of pure water in the other. This conclusion is strengthened by Mr. Graham's observation, that common salt diffuses into water, through a thin membrane of ox-bladder deprived of its outer muscular coating, at the same rate as when no membrane is interposed.

The flow of water into the saline solution is the only one of the two movements which can be correctly described as a current. This is, in fact, the true osmose, and depends es-

sentially on the action of the membrane or other porous septum; for the quantity of water which thus passes into the solution, is often much greater than would be introduced by mere liquid diffusion, amounting in some cases to several hundred times that of the salt displaced.

This action of the septum has been explained in various ways. By Dutrochet and others, it was attributed to capillarity; but this force is quite insufficient to account for the great inequality of ascension which different liquids exhibit in the osmotic apparatus; in fact, Mr. Graham has shown, that solutions of the most different character exhibit very nearly equal ascension in tubes of equal diameter.

Osmose has likewise been attributed to the unequal absorption of the two liquids by the porous septum. Suppose the septum to be of such a nature as to absorb only one of the liquids, the water for instance. The water will then penetrate the septum, and coming in contact with the saline solution, will diffuse into it. More water will then be absorbed, and subsequently diffused, and thus a continuous current will be set up. If both liquids are absorbed by the septum, but in different degrees, and each is capable of diffusing into the other, like water and alcohol, the result will be the formation of two unequal currents in opposite directions. Water is absorbed by animal membrane much more rapidly than most other liquids, and accordingly, when a septum of this kind is used, the direction of the current is in most cases from the water to the other liquid. According to Liebig, a given weight of dried ox-bladder absorbs in the same time, 200 volumes of water, 133 vols. of a saturated solution of common salt, 38 vols. of alcohol of the strength of 84 per cent., and 17 vols. of bone-oil. When water and alcohol are separated by an animal membrane, the quantity of water which passes into the alcohol, is greater than the quantity of alcohol which passes into the water; but when the same liquids are divided by a thin film of collodion, which absorbs alcohol more quickly than water, the contrary effect is produced.

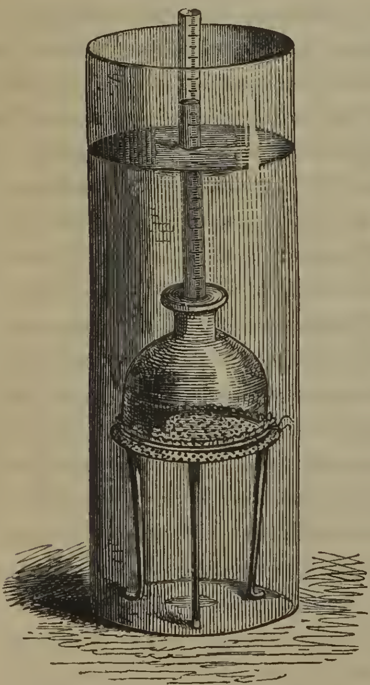
On the other hand, the numerous experiments recently made by Mr. Graham *, lead to the conclusion, that osmose depends essentially on the chemical action of the liquid on the septum. These experiments were made partly with porous mineral septa, partly with animal membrane. The earthenware osmometer consisted of the porous cylinders employed in voltaic batteries, about five inches in depth, surmounted by a glass tube 0·6 inch in diameter, attached to the mouth of the cylinder by means of a cap of gutta percha. The cylinder was filled to the base of the glass tube with a saline solution, and immediately placed in a jar of distilled water; and as the fluid within the instrument rose during the experiment, water was added to the jar to equalise the pressure. The rise (or fall) of the liquid in the tube was very regular, as observed from hour to hour, and the experiment was generally terminated in five hours. From experiments made on solutions of every variety of soluble substance, it appeared that the rise or osmose, is quite insignificant with neutral organic substances in general, such as sugar, alcohol, urea, tannin, &c.; so likewise with neutral salts of the earths and ordinary metals, with the chlorides and nitrates of potassium and sodium, and with chloride of mercury. A more sensible but still very moderate osmose is exhibited by hydrochloric, nitric, acetic, sulphurous, citric, and tartaric acids. These are surpassed by the stronger mineral acids, such as sulphuric and phosphoric, and by sulphate of potash, which are again exceeded by salts of potash and soda possessing a decided acid or alkaline reaction, such as binoxalate of potash, phosphate of soda, or the carbonates of potash and soda. The highly osmotic substances were also found to act with most advantage in small proportions, producing, in fact, the largest osmose in the proportion of one-quarter per cent. dissolved. (See page 621.) The same substances are likewise always chemically active bodies, and possess affinities which enable them to act on the

* Phil. Trans. 1855, 177; Chem. Soc. Qu. J. viii. 43.

material of the earthenware septum. Lime and alumina were always found in solution after osmose, and the corrosion of the septum appeared to be a necessary condition of the flow. Septa of other materials, such as pure carbonate of lime, gypsum, compressed charcoal, and tanned sole-leather, although not deficient in porosity, gave no osmose, apparently because they are not chemically acted on by the saline solutions.

Similar results were obtained with septa of animal membrane. Ox-bladder was found to act with much greater strength and regularity when divested of its outer muscular coat. Cotton-calico, impregnated with liquid albumen, and afterwards heated to coagulate the albumen, formed an excellent septum, resembling membrane in every respect. The osmometer (Fig. 45) used in these experiments was arranged like the original instrument of Dutrochet; but the membrane was supported by a plate of perforated zinc, and the tube was of considerable diameter, viz. one-tenth of that of the mouth of the bulb, or of the disc of membrane exposed to the liquids.

Fig. 45.



Osmose in membrane presents many points of similarity to that in earthenware. The membrane is constantly undergoing decomposition, and its osmotic action is exhaustible. Salts and other substances capable of determining a large osmose, are all che-

mically active substances, while the great mass of neutral organic substances and perfectly neutral monobasic salts of the metals, such as chloride of sodium, possess only a low degree of action, or are wholly inert. The active substances are also most efficient in small proportions.* With a solution containing $\frac{1}{10}$ per cent. of carbonate of potash, the rise in the osmometer was 167 millimeters; and with 1 per cent. of the same salts, 206 millimeters in five hours. With another membrane and a stronger solution, the rise was 863 millimeters, or upwards of 38 inches, in the same time. To induce osmose, the chemical action on the membrane must be different on the two sides, and apparently not in degree only, but in kind, viz. an alkaline action on the albuminous substance of the membrane on the one side, and an acid action on the other. The water appears always to accumulate on the alkaline or basic side of the membrane. Hence, with an alkaline salt, such as carbonate of soda, in the osmometer, and water outside, the flow is inwards; but with an acid in the osmometer, there is negative osmose, or the flow is inwards, the liquid then falling in the tube. The chlorides of barium, sodium, and magnesium, and similar neutral salts, are wholly indifferent, or appear to act merely in a subordinate manner to some other active acid or basic substance, which may be present in the solution or the membrane in the most minute quantity. Salts which admit of division into a basic salt and free acid, exhibit an osmotic activity of the highest order, *e. g.* the acetate and various other salts of alumina, ferric oxide and chromic oxide, dichloride of copper, proto-chloride of tin, nitrate of lead, &c. The acid travels outwards by diffusion, superinducing a basic condition of the inner surface of the membrane, and an acid condition of the

* The action increases with the strength of the solution up to a certain point, as the above examples show (see also p. 619). With stronger solutions the pores of the membrane probably become stopped up with particles of salt, and the action consequently diminishes.

outer surface, the most favourable condition for a high positive osmose. Again, the bibasic salts of potash and soda, such as the sulphate and tartrate, though strictly neutral in properties, begin to exhibit a positive osmose, in consequence, perhaps, of their resolution into an acid supersalt and free alkaline base.

The following table exhibits the osmose of substances of all classes through membrane, the degree being a rise or fall of one millimeter : —

Osmose of 1 per Cent. Solutions in Membrane.

	Degrees.		Degrees.
Oxalic acid	−148	Chloride of zinc	+54
Hydrochloric acid (0·1 per cent.)	−92	Chloride of nickel	88
Terchloride of gold	−54	Nitrate of lead	125 to 211
Bichloride of tin	−46	Nitrate of cadmium	137
Bichloride of platinum	−30	Nitrate of uranium	234 to 458
Chloride of magnesium	−3	Nitrate of copper	204
Chloride of sodium	+2	Chloride of copper	351
Chloride of potassium	18	Protochloride of tin	289
Nitrate of soda	2	Protochloride of iron	435
Nitrate of silver	34	Chloride of mercury	121
Sulphate of potash	21 to 60	Mercurous nitrate	356
Sulphate of magnesia	14	Mercuric nitrate	476
Chloride of calcium	20	Ferric acetate	194
Chloride of barium	21	Acetate of alumina	280 to 393
Chloride of strontium	26	Chloride of aluminium	540
Chloride of cobalt	26	Phosphate of soda	311
Chloride of manganese	34	Carbonate of potash	439

The osmotic action of carbonate of potash and other alkaline salts is interfered with in an extraordinary manner by the presence of chloride of sodium, being reduced to almost nothing by an equal proportion of that salt. The moderate positive osmose of sulphate of potash is converted into a very sensible negative osmose by the presence of the merest trace of a strong acid, while the positive osmose of the same salt is singularly promoted by a small proportion of alkaline carbonate: thus a 1 per cent. solution of sulphate of potash gives an osmose of 21 degrees, but the addition of 0·1 per cent. of

carbonate of potash raises it to between 254 and 264 degrees. (Graham.)

If a glass tube, bent in the form of a siphon, and having its shorter leg closed with bladder, be partially filled with salt-water, the shorter leg then immersed in a vessel of pure water, and mercury poured into the longer leg, so that its pressure may act in opposition to the force with which the water tends to enter the saline solution through the bladder, it will be found that, when the column of mercury attains a certain height, the two liquids will mix without change of volume, the force of the osmotic current being then exactly balanced by the weight of the mercurial column. In this way the mechanical force of the osmotic current may be measured. (Liebig.)

Osmose appears to play an important part in the functions of life. We have seen that it is peculiarly excited by dilute saline solutions, such as the animal and vegetable juices are, and that the acid or alkaline property which these juices possess is another favourable condition for their action on membrane. The natural excitation of osmose in the substance of the membranes or cell-walls dividing such solutions seems therefore almost inevitable.

In osmose there is also a remarkably direct substitution of one of the great forces of nature by its equivalent in another force, the conversion, namely, of chemical action into mechanical power. Viewed in this light, the osmotic injection of fluids may, perhaps, supply the deficient link which intervenes between chemical decomposition and muscular movement. The ascent of the sap in plants appears to depend upon a similar conversion of chemical, or, at least, molecular action into mechanical force. The juices of plants are constantly permeating the coatings of the superficial vessels in the leaves and other organs; and these evaporating into the air, a fresh portion of liquid is then absorbed by the membrane and evaporates; and thus a regular upward current

is established, by which the sap is transferred from the roots to the highest parts of the tree. In a similar manner, the evaporation constantly taking place from the skin and lungs of animals, causes a continuous flow of the animal juices from the interior towards the surface.

DIFFUSION OF GASES THROUGH POROUS SEPTA.

It appears from Mr. Graham's experiments (I. 87), that the rates of diffusion of gases through porous diaphragms, such as dry gypsum, cork, unglazed earthenware, or bladder, are to one another in the inverse ratio of the squares of their densities, the law being, in fact, the same as that of the *effusion* of the same gases into a vacuum through minute apertures in a metal plate (I. 78). Bunsen has arrived at a different conclusion.* He finds, for example, that when a tube containing hydrogen is closed by a dry gypsum diaphragm, and a current of oxygen passed rapidly over the diaphragm, so that the hydrogen may diffuse into an infinite atmosphere of oxygen, the volume of oxygen which enters the tube is to the volume of hydrogen which issues from the tube, as 1 : 3·345, this ratio remaining constant during the whole time of the diffusion. The law of the inverse square roots of the densities would give 1 : 4. Again, when oxygen was made to pass through stucco into oxygen, and hydrogen into hydrogen, by difference of pressure, it was found that, under the same pressure, the rate of issue of the oxygen was to that of the hydrogen as 1 : 2·73 instead of 1 : 4. These differences are too great to be accounted for by error of observation; they probably arise from the circumstance, that Graham's experiments were made with thin diaphragms, whereas Bunsen used diaphragms of considerable thickness†, in which case, the rates of diffusion would approximate to the rates of

* See Bunsen's "Gasometry," translated by Dr. Roscoe, pp. 198—233.

† Compare the figure at page 87, Vol. I., of this work, with figure 53, p. 202. of Bunsen's "Gasometry."

transpiration (I. 82.) rather than to those of effusion. The rate of transpiration through a mass of porous stucco was ascertained by Mr. Graham to be the same as through capillary tubes, namely, 1 volume of oxygen to 2·3 volumes of hydrogen. In the interior of a considerable mass of stucco, with hydrogen on one side and oxygen on the other, the stucco acts as a vessel, a partial vacuum being formed in its centre. To this point, both oxygen and hydrogen are impelled by pressure (transpiration) in the ratio of 1 to 2·3, instead of 1 to 4, the relation of diffusion. Hence the oxygen travels through the diaphragm, partly in one of these ratios and partly in the other, and the proportion of oxygen which enters the vessel is increased, as in Bunsen's experiments.*

DEVELOPMENT OF HEAT BY CHEMICAL ACTION.

From the time when Lavoisier pointed out the true nature of the phenomenon of combustion, the measurement of the heat evolved in chemical combination has occupied a prominent place in the attention of chemists, and has been made the subject of numerous researches, the most exact and comprehensive of which, are those of Messrs. Favre and Silbermann, and of Dr. Andrews.†

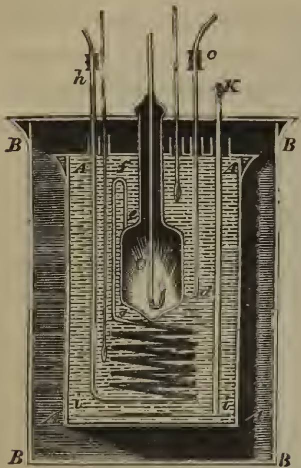
The apparatus used by Favre and Silbermann for measuring the heat evolved by the combustion of various substances in oxygen gas, is represented, with the omission of minor details, in figure 46. *C* is a vessel of gilt brass plate, immersed in a water-calorimeter, *A A*, of silvered copper-plate, and the latter is enclosed in an outer vessel, *B B*, the space between *A* and *B* being filled with swan-down, to prevent the escape of heat from the water in *A*. The vessels *A* and *B* are closed

* Ann. Ch. Phys. [3], xxxiv. 357 ; xxxvi. 5; xxxvii. 405 ; Abstr. Chem. Soc. Qu. J. vi. 234.

† Phil. Mag. [3], xxxii. 321, 392, and 426.

with lids having apertures for the insertion of tubes and thermometers. The combustions are performed in the vessel

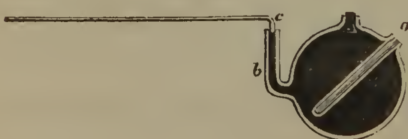
FIG. 46.



C, into which oxygen gas is introduced through the tube *c d*, and the gaseous products of the combustion escape by the tube *e f g h*, the lower part of which is bent into numerous coils, to facilitate as much as possible, the transmission of the heat of these gases to the water in the calorimeter. The extremity *h*, of this tube is connected with a gasometer, or with an absorbing apparatus. To ensure uniformity of temperature in the water, a flat ring of metal *i i*, is moved up and down by means of the rod *K i*. Combustible gases were introduced into the vessel *C*, by means of fine tubes, the gas being previously set on fire at the aperture. Solid bodies were attached to fine platinum wires suspended from the lid of the calorimeter: liquids were burned in small capsules or in lamps with asbestos wicks; charcoal was disposed in a layer on a sieve-formed bottom, through the openings of which the oxygen had access to it. The heat evolved was measured by the rise of temperature of the known quantity of water in the calorimeter.

For processes which take place without access or escape of gases, simpler apparatus may be used. For such reactions Favre and Silbermann employed a *mercury-calorimeter*, (Fig. 47),

FIG. 47.



consisting of a glass globe filled with mercury, and having inserted into it a tube *a*, to contain the combining

substances, an acid and a base for instance. The mercury in the globe communicates by the bent tube *b*, with the capillary tube *c d*, on which its expansion is measured. The apparatus forms, in fact, a large mercurial thermometer.

The unit of weight to which the following numbers refer is the gramme, and the unit of heat is the quantity required to raise the temperature of 1 gramme of water from 0° to 1° C.

Substance.	Formula.	Products.	Heat of Combustion. 1 Grm. of Substance with Oxygen.	Heat of Combustion. 1 Grm. of Oxygen with Substance.	Observers.
GASES.					
Hydrogen	HH	H_2O	34462	4308	F. S.
			33802	4226	A.
Carbonic oxide . . .	CO	CO_2	2403	4205	F. S.
			2431	4255	A.
Marsh-gas	CH_4	CO_2 and H_2O	13063	3266	F. S.
			13168	3277	A.
Olefiant-gas	C_2H_4	"	11858	3458	F. S.
			11942	3483	A.
LIQUIDS.					
Amylene	C_5H_{10}	"	11491	3352	F. S.
Oil of turpentine . . .	$C_{10}H_{16}$	"	10852	3294	"
Ether	$C_4H_{10}O$	"	9028	3479	"
Wood-spirit	CH_4O	"	5307	3538	"
Alcohol	C_2H_6O	"	7184	3442	"
Amylic alcohol . . .	$C_5H_{12}O$	"	8959	3285	"
Acetic acid	$C_2H_4O_2$	"	3505	3286	"
Butyric acid	$C_4H_8O_2$	"	5647	3106	"
Valerianic acid . . .	$C_5H_{10}O_2$	"	6439	3158	"
Palmitic acid (solid) .	$C_{16}H_{32}O_2$	"	9316	3240	"
Stearic acid (solid) . .	$C_{18}H_{36}O_2$	"	9716	3317	"
Formiate of methyl . .	$C_2H_4O_2$	"	4197	3935	"
Acetate of methyl . .	$C_3H_6O_2$	"	5342	3529	"
Formiate of ethyl . .	$C_3H_6O_2$	"	5279	3488	"
Acetate of ethyl . . .	$C_4H_8O_2$	"	6293	3461	"
Butyrate of methyl . .	$C_5H_{10}O_2$	"	6791	3334	"
Butyrate of ethyl . .	$C_6H_{12}O_2$	"	7091	3213	"
Valerate of methyl . .	$C_6H_{12}O_2$	"	7376	3342	"
Spermaceti (solid) . .	$C_{32}H_{64}O_2$	"	10342	3301	"
Sulphide of carbon . .	CS_2	CO_2 and SO_2	3401	2692	"

Substance.	Formula.	Products.	Heat of Combustion.		Observers.
			1 Grm. of Substance with Oxygen.	1 Grm. of Oxygen with Substance.	
SOLIDS.					
Carbon (wood-charcoal)	$\cancel{C}$	$\cancel{C}\cancel{O}$	2473	1855	F. S.
		$\cancel{C}\cancel{O}_2$	8080	3030	"
Sulphur (rhombic) . .	$\cancel{S}$	$\cancel{S}\cancel{O}_2$	2221	2221	"
Phosphorus (yellow) .	PP	$P_2\cancel{O}_5$	5953	4613	"
Zinc	ZnZn	$Zn_2\cancel{O}$	1301	5366	A.
Iron	FeFe	$Fe_3\cancel{O}_2$	1575	4134	"
Tin	SnSn	$Sn\cancel{O}$	1167	4230	"
Protoxide of tin . . .	$Sn_2\cancel{O}$	$Sn\cancel{O}$	521	4349	"
Copper	CuCu	$Cu_2\cancel{O}$	604	2394	"
Red oxide of copper .	$Cu_4\cancel{O}$	$Cu_2\cancel{O}$	256	2288	"

A comparison of the numbers in this Table, shows that the quantities of heat evolved by the combination of a constant weight of oxygen with different combustible bodies, are much more nearly equal than the quantities evolved by the combustion of equal weights of these several bodies. Nevertheless, the conclusion drawn from older experiments (I. 300), that the quantity of heat evolved in combustion is always proportionate to the quantity of oxygen consumed, is very far from being confirmed by the numbers in the fifth column of the preceding Table.

Equal weights of isomeric bodies do not evolve equal quantities of heat in combustion. This may be seen by comparing the numbers for formiate of ethyl and acetate of methyl, for acetic acid and formiate of methyl, &c.

In homologous organic compounds, the heat of combustion for equal weights of the compounds increases, as the carbon and hydrogen bear a greater proportion to the oxygen. This may be seen in the series of alcohols, fatty acids, and compound ethers.

In general, the heat evolved by the combustion of an oxidised body, such as carbonic oxide, or protoxide of tin, is less

than that which is evolved in the complete oxidation of the combustible constituent.

But little is known respecting the relation which the heat of combustion of a compound of two or more combustible substances bears to the sum of the heats of combustion of its constituents. In some cases, it is less than that sum (*e. g.* marsh-gas and olefiant gas); in others, greater (bisulphide of carbon, oil of turpentine). The relation in question is, doubtless, greatly affected by the molecular states of the compound and of its elements in the separate state. That the heat of combustion of a body is materially influenced by its state of aggregation, is shown by many experiments; and in general it is found that, of two modifications of a substance, that which has the greater specific heat, likewise evolves the greater quantity of heat in combination. Thus, the specific heat of yellow phosphorus is greater than that of the red variety; now 1 gramme of yellow phosphorus, in burning to phosphoric acid, evolves 5953 heat-units, whereas the same quantity of red phosphorus evolves only 5070 heat-units. The same relation is strikingly shown by the following comparison of the quantities of heat evolved in the complete combustion of equal weights of different kinds of carbon, as determined by Favre and Silbermann, with their specific heats, as determined by Regnault:—

	Heat of Combustion.	Specific Heat.
Wood-charcoal	8080	0·24150
Coke from gas-retorts	8047	0·20360
Native graphite	7797	0·20187
Graphite from blast-furnaces	7762	0·19702
Diamond	7770	0·11687

Sulphur likewise evolves in combustion different quantities of heat, according to its state of aggregation. Octohedral sulphur, native or artificial, gives, as a mean result, 2221 heat-

units; prismatic sulphur, recently crystallised from fusion, gives 2260 heat-units.

Combination of Metals with Chlorine, Bromine, and Iodine.—To determine the heat evolved in the combination of metals with chlorine, Andrews introduced the metals, enclosed in thin glass bulbs, into a glass vessel filled with dry chlorine. This vessel was placed within the water-calorimeter, and the glass bulb broken by shaking the vessel. The results are given in the following Table. The number for hydrogen is from the experiments of Favre and Silbermann:—

Substance.	Product.	Heat of Combustion.	
		1 Gramme of Substance with Chlorine.	1 Gramme of Chlorine with Substance.
Hydrogen . . .	HCl	23783	670
Potassium . . .	KCl	2655	2932
Zinc	ZnCl	1529	1404
Copper	CuCl	961	858
Iron	Fe_2Cl_3	1745	317
Tin	$SnCl_2$	1079	881
Arsenic	$AsCl_3$	994	700
Antimony . . .	$SbCl_3$	707	799

If we multiply the numbers which express the heat of combination of 1 gramme of each of the metals with oxygen and chlorine, by the atomic weights of the several metals, we obtain the following numbers for the quantities of heat evolved by equivalent quantities of these metals in combining with oxygen and chlorine:—

	With 8 gr. Oxygen.	With 35·5 gr. Cl.
1 gramme of hydrogen	34462	23783
32·6 „ zinc	42413	49844
31·7 „ copper	19147	30464
29 „ tin (to SnO and $SnCl_2$) .	33843	31291

The numbers in this Table do not exhibit any simple relation to each other, so that no conclusion can be drawn from them as to the quantity of heat evolved or absorbed in the

substitution of chlorine for oxygen, or of one metal for another in combination with either of these elements. Here, as in other cases, the difference in the state of aggregation doubtless interferes with the constancy of action which might otherwise be observed. The amount of interference arising from this cause is much diminished when compounds are compared in the state of aqueous solution; and accordingly it is found that, when the quantities of heat evolved by the combination of different bases and acids (or metals and radicals), in the form of soluble salts, are compared, numbers are obtained which exhibit a tolerably near approach to regular progression.

The following Table exhibits the number of units of heat evolved by equivalent quantities of different bases in combining with various acids, as determined by Favre and Silbermann:—

Bases.	Acids.					
	Sulphuric.	Nitric.	Hydrochloric.	Hydrobromic.	Hydriodic.	Acetic.
Grm.						
47·2 Potash	16083	15510	15656	15510	15698	13978
31 Soda	15810	15283	15128	15159	15097	13600
26 Oxide of ammonium	14690	13676	13536			12649
76·5 Baryta		15360	15306			13262
28 Lime		16943	16982			14675
20 Magnesia	14440	12840	13220			12270
35·6 Manganous oxide	12075	10850	11235			9982
40·6 Zinc-oxide	10455	8323	8307			7720
64 Cadmic oxide	10240	8116	8109			7546
39·7 Cupric oxide	7720	6400	6416			5264
37·6 Nickel-oxide	11932	10450	10412			9245
37·5 Cobaltous oxide	11780	9956	10374			9272
111·7 Lead-oxide		9240				7168
116·1 Silver-oxide		6206				

A comparison of these numbers shows that nitric, hydrochloric, hydrobromic, and hydriodic acids, in combining with the same base, evolve nearly equal quantities of heat; sul-

phuric acid a considerably greater, and acetic acid a smaller quantity. Among the bases, the alkalies evolve the greatest quantity of heat in combining with any acid. In general, it appears that the greatest heat is evolved by the combination of the strongest acids with the strongest bases.

The corresponding terms of any two horizontal rows in the preceding table exhibit, in some cases, nearly equal differences; and the same is true with regard to the corresponding terms of any two vertical rows. If these differences were constantly equal, it would follow that the quantities of heat evolved or absorbed in the substitution of a base *a* for a base *b* (potash for soda, for example), would be the same with whatever acid the base were united; and, similarly, the heat evolved or absorbed in the substitution of one particular acid for another, would be independent of the bases. The actual differences, however, deviate too much from this law to warrant its reception as an expression of the results of observation. Nevertheless, there is a considerable degree of *à priori* probability in its favour; and the observed deviations from it may perhaps arise from disturbing causes, such as the different quantities of heat absorbed in the solution of salts, &c. How far this is the case, remains to be decided by further experiments.

Heat is likewise evolved in the combination of acids with water. The following are the quantities of heat developed, according to Favre and Silbermann, by mixing sulphuric acid, SO_4H, with various proportions of water.

	Heat-units.	Differences.
With the first $\frac{1}{8}$ atom water	9·4	0·6
second $\frac{1}{8}$,, ...	8·8	
first $\frac{1}{4}$,, ...	18·8	1·6
second $\frac{1}{4}$,, ...	17·2	
first $\frac{1}{2}$,, ...	36·7	8·4
second $\frac{1}{2}$,, ...	28·3	

	Heat-units.	Differences.
With 1 atom water	64·7	
2 „	94·6	29·9
3 „	111·9	17·3
4 „	122·2	10·3
5 „	130·7	8·5
6 „	136·2	5·5
7 „	141·8	4·4
8 „	145·1	3·3
9 „	148·5	3·4
10 „	148·4	0·0
20 „	148·6	0·0

These numbers show that the heat evolved by adding a given quantity of water to hydrated sulphuric acid, diminishes as the quantity of water already present is greater.

Heat evolved by the solution of gases in water. — When a gas dissolves in water, heat is evolved, partly in consequence of the chemical combination, and partly from the condensation of the gas to the liquid state. According to Favre and Silbermann: —

	Heat-units.
1 gramme of hydrochloric acid gas dissolved in water evolves	449·6
1 „ hydrobromic „ „ „	235·6
1 „ hydriodic „ „ „	147·7
1 „ sulphurous „ „ „	120·4
1 „ ammoniacal gas „ „ „	514·3

The heat evolved varies, however, according to the quantity of water in which a given quantity of the gas dissolves.

Solution of salts, &c., in water. — The calorific effect produced by the solution of a solid in a liquid, depends upon several circumstances; viz. on the chemical affinity between the two, on the quantity of heat absorbed in the passage of the solid to the liquid state, on the quantity of the solvent, and on the temperature at which the solution takes place. The result is, in most cases, an absorption of heat or reduction of temperature; in some cases, however, as when the act of solution is preceded or accompanied by the formation of a definite hydrate, the effect may be reversed. The combination of anhydrous potash with water to form the hydrate

KO . HO, is attended with a rise of temperature sufficient to produce incandescence; the hydrate KO . HO likewise evolves a considerable quantity of heat on dissolving in water, because it first combines with a definite proportion of water, forming the hydrate $KHO_2 . 4HO$; but the solution of this latter compound in water produces a considerable fall of temperature. Anhydrous chloride of calcium combines with water, forming the hydrate CaCl . 6HO, the combination being attended with great evolution of heat; but the solution of the hydrate in water produces cold.

The absorption of heat accompanying the solution of salts is not wholly due to the liquefaction of the solid; for the heat thus absorbed in solution is sometimes greater, sometimes less than when the salt is liquefied by heat alone. Thus, in the fusion of 1 gramme of nitrate of potash, 49 heat-units are rendered latent; but when the same salt is dissolved in 20 parts of water, at 20° C., 80 heat-units are absorbed. The latent heat of fusion of crystallised chloride of calcium is 41 heat-units; but when this hydrated salt dissolves in 12 parts of water at 8° C., only 19 heat-units are absorbed. (C. Person.*)

The following results are extracted from Person's determinations of the influence of the temperature and quantity of the solvent on the quantity of heat absorbed:—

Name of Salt.		Quantity of Water.	Temperature.	Units of Heat absorbed.
Chloride of sodium . .	1 gramme	7·28	17·1 C.	13·5
		7·28	10·3	14·9
		7·28	0·2	18·7
Nitrate of soda . . .	"	5	22·7	47·1
		20	22·8	55·7
Nitrate of potash . .	"	10	23·8	76·7
		10	5·5	80·2
		20	5·7	86·4
		20	19·7	80·5

* Ann. Ch. Phys. [3], xxxiii. 448.

Hence it appears that when a given quantity of a salt is dissolved in the same quantity of water at different temperatures, the quantity of heat absorbed is greater as the initial temperature is lower; and at the same temperature, the quantity of heat absorbed increases with the quantity of the solvent. A fall of temperature is sometimes produced by merely diluting a solution with water. (Person.)

COLD PRODUCED BY CHEMICAL DECOMPOSITION.

The separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination. The truth of this proposition has been established by Dr. Woods * and Mr. Joule †, by comparing the heat evolved in the electrolysis of water, with that which is developed in a thin metallic wire by a current of the same strength. The current was first made to pass through a vessel containing acidulated water, the quantity of gas evolved in a given time determined, and also the rise of temperature, the strength of the current being at the same time measured by the tangent-compass (p. 497). The electrolytic cell was then removed, and a thin platinum wire introduced between the poles, of such a length as to produce a resistance equal to that of the electrolyte. The quantity of heat evolved in this wire was then determined, and found to exceed that which was previously evolved in the electrolytic cell, by a quantity equal to that which would be evolved in the combination of the oxygen and hydrogen eliminated by the current in the previous experiment.

The same proposition is likewise established by many other chemical phenomena. When zinc dissolves in dilute sulphuric acid, the action may be supposed to consist of three stages, viz. the decomposition of water, the formation of oxide of

* Phil. Mag. [4], ii. 368.

† Phil. Mag. [4], iii. 481.

zinc, and the combination of the oxide of zinc with sulphuric acid, forming $ZnO \cdot SO_3$. Now:

	Heat-units.
The heat evolved in the oxidation of 1 atom or 32·6 parts of zinc .	= 42413
The heat evolved in the combination of 1 atom or 40·6 parts oxide of zinc with sulphuric acid, in presence of a large quantity of water (p. 631)	= 10455
Sum .	= 52868
Deducting from this the heat evolved in the combination of 1 atom or 1 gramme of hydrogen with oxygen	= 34462
There remains for the heat evolved in the entire process . .	18406

which agrees very nearly with the quantity determined by direct experiment, viz. 18,514 heat-units.

Again, when metallic oxides are reduced by hydrogen, the heat evolved is not so great as when the same quantity of hydrogen combines with free oxygen, because it is diminished by the heat absorbed in the separation of the oxygen and the metal.

The reduction of oxide of iron by hydrogen takes place without much evolution of heat, because the heat evolved in the combination of 1 grm. of oxygen with hydrogen, viz. 4308 heat-units (p. 627), is not much greater than that which is evolved when the same quantity of oxygen combines with iron, viz. 4134 heat-units. But the reduction of oxide of copper is attended with a rise of temperature amounting to incandescence, because the heat evolved in the oxidation of hydrogen greatly exceeds that which is evolved in the oxidation of copper, which is only 2393 heat-units.

The absorption of heat in decomposition is also demonstrated by the fact that no alteration of temperature takes place in the double decomposition of salts, provided all the products remain in solution; in fact, the heat evolved in the combinations is exactly compensated by the cold produced by the decompositions which take place at the same time. But if a precipitate is formed, heat is evolved, in consequence of

the passage of the compound from the liquid to the solid state.

There are some phenomena which appear to contradict the assertion that heat is always absorbed in chemical decomposition. The decomposition of some of the oxides of chlorine, and of the chloride and iodide of nitrogen, is attended with evolution of heat. It has also been shown by Favre and Silbermann, that, in the combustion of charcoal in nitrous oxide, more heat is evolved than when charcoal burns in pure oxygen; and that the decomposition of peroxide of hydrogen by platinum is attended with considerable rise of temperature. These apparent anomalies may, however, be reconciled with the general law, if we admit that all chemical actions may be regarded as double decompositions (pp. 517—520). Thus, in the last case, regarding peroxide of hydrogen as water *plus* oxygen, the decomposition may be represented by the equation: —

$$HO.O + HO.O = 2HO + OO.$$

And it is possible that the heat evolved in the combination of oxygen with oxygen, may be greater than that which is absorbed in the separation of the oxygen from the water; and similarly in the other cases.

NON-METALLIC ELEMENTS.

OXYGEN AND HYDROGEN.

Extraction of Oxygen from Atmospheric air.—Boussingault has shown* that it is possible to obtain oxygen gas in considerable quantity from the air by the use of baryta, that substance absorbing oxygen from the air at a low red heat, and being converted into peroxide of barium, and the latter, when raised to a higher temperature,—or still more easily when exposed to a current of aqueous vapour,—giving up its second atom of oxygen in the free state. The apparatus used consists of a tube of porcelain or glazed earthenware, communicating at the one end, by means of smaller tubes provided with stopcocks, with an aspirator and a gas-holder, and at the other with the external air and also with a steam-boiler. The tube is filled with hydrate of baryta,—mixed with lime or magnesia to diminish its fusibility,—and heated to low redness, a current of air being at the same time drawn through the tube by the aspirator. The hydrate of baryta is thereby converted into peroxide of barium; and when the oxidation has proceeded far enough, the current of air is suspended, a jet of steam sent through the tube, and at the same time the connection with the gas-holder is opened; the peroxide of barium is then reconverted into hydrate of baryta, and the excess of oxygen passes into the gas-holder. The hydrate of

* Compt. rend. xxxii. 261; Ann. Ch. Phys. [3], xxx. 5; Chem. Soc. Qu. J. v. 269.

baryta may now be reoxidised by a fresh current of air, the resulting peroxide again decomposed by vapour of water, — and this series of operations may be repeated any number of times. Boussingault's first experiments were made with anhydrous baryta, which likewise absorbs oxygen when heated to low redness in a current of air, and gives it up again at a bright red heat. It was found, however, that the baryta, after one or two repetitions of the process, lost in a great measure its power of absorbing oxygen. In fact, baryta, when really anhydrous, shows but little inclination to absorb oxygen; it is only the hydrate that is readily converted into BaO_2. Now baryta, when prepared in the ordinary way, by calcining the nitrate, always contains a little water, which facilitates the absorption of the oxygen; but after being heated two or three times in a current of dry air, it becomes really anhydrous, and is then no longer oxidised. The use of hydrate of baryta is therefore much more advantageous, both for the reason just stated, and likewise because the decomposition of the peroxide by vapour of water takes place at a much lower temperature than by simple ignition. The process in this form is adapted for use on the large scale.*

Ozone (I. 304). — The nature of ozone is still a matter of discussion. That it is a higher oxide of hydrogen was first suggested by Professor Williamson †, who passed ozoniferous oxygen, obtained by electrolysis, first over chloride of calcium to dry it, and then through a glass tube, in which it was either heated by a spirit-lamp or brought in contact with finely

* A patent for the preparation of oxygen in this manner, and its application in various chemical operations, has been taken out by Messrs. Swindells and Nicholson. (Chem. Gaz. 1855, 139.)

† Ann. Ch. Pharm. liv. 127. This view was afterwards adopted by Schönbein (*Pogg. Ann.* lxvii. 78), but he has since abandoned it, inclining rather to regard ozone as an allotropic modification of oxygen (*Ann. Ch. Pharm.* lxxxii. 222; *J. pr. Chem.* liii. 65).

divided copper at a red heat. The ozone was thereby decomposed and deprived of its odour, and water was deposited. The same view has been further supported by the more recent experiments of Baumert*, who has likewise analysed the ozone quantitatively, and finds that it is a *teroxide of hydrogen*, HO_3. In Baumert's experiments, ozoniferous oxygen, evolved at the positive pole from water acidulated with sulphuric and chromic acids (which mixture was found to yield the largest quantity of ozone, not, however, exceeding 1 milligramme of that substance to $3\frac{1}{3}$ litres of oxygen) was passed, after thorough drying, into a glass tube lined with a film of anhydrous phosphoric acid. On heating the tube with a spirit-lamp, the phosphoric acid became transparent, and was dissolved at the part of the tube beyond the flame, showing that water was there deposited. It would appear then that ozone, obtained by electrolysis, contains the elements of water; and its powerful oxidising properties show that it also contains an excess of oxygen. Hence, to analyse it quantitatively, it is only necessary to determine the proportion of this excess of oxygen in a known weight of ozone. The analysis was made by passing the ozoniferous oxygen, first through a tube containing pumice-stone soaked in sulphuric acid, to dry it; then through a bulb-apparatus containing solution of iodide of potassium, which completely absorbed the ozone, and was itself at the same time partially decomposed, a certain quantity of iodine being set free by the excess of oxygen in the ozone; and, lastly, through a second bulb-apparatus containing strong sulphuric acid, to absorb any water mechanically carried forward from the iodide of potassium solution by the stream of gas. The increase of weight in the two bulb-apparatus gave the total quantity of ozone; and the quantity of iodine set free (estimated by Bunsen's volumetric method†)

* Pogg. Ann. lxxxix. 38; Chem. Soc. Qu. J. vi. 169.
† Ann. Ch. Pharm. lxxxvi. 265.

determined the amount of active oxygen therein. Two experiments made in this manner gave in 100 parts of ozone:—96·24 O + 3·76 H, and 95·70 O + 4·30 H respectively. The formula, HO_3, requires 95·66 O + 4·34 H. The oxidising action of the ozone was found to be so powerful, that it quickly destroyed any organic substance, such as vulcanised caoutchouc, used to connect the different parts of the apparatus: hence it was necessary to make all the connections either by fusion or by grinding.

Baumert has also found, in accordance with the observations of previous experimenters, that perfectly dry oxygen gas, subjected for some time to the action of the electric spark, is brought into an allotropic state, in which its combining tendencies are highly exalted, so that it is capable of overcoming the most powerful affinities, such as that of chlorine or iodine for potassium, at ordinary temperatures. Ozonised oxygen was freed from ozone and aqueous vapour by passing through sulphuric acid, through a heated glass tube, over fragments of iodide of potassium, and through pulverulent phosphoric acid, and then made to pass through a glass tube having platinum wires fixed into its sides. On passing a rapid succession of electric sparks between these wires, the gas acquired again the odour of ozone, and the power of decomposing a solution of iodide of potassium, characters which it did not possess before the sparks were passed through it. When heated to 200° C. it lost these peculiar properties, and was restored to its ordinary state. Results similar to this had previously been obtained by Marignac and De la Rive, and also by Fremy and Becquerel.* In the experiments of the last-mentioned philosophers, perfectly dry oxygen gas, enclosed in sealed glass tubes, and subjected to the continued action of electric sparks passed along the *outer* surface of the glass, was found to acquire the power of decomposing iodide of potassium,

* Ann. Ch. Phys. [3], xxxv. 62; Chem. Soc. Qu. J. v. 272.

and was absorbed by moist mercury or silver, and by solution of iodide of potassium. From these experiments it may be reasonably concluded that oxygen can by certain means be brought into a modified and excited condition; but as this modified oxygen, when it exhibits the odour of ozone, or any of its peculiar reactions, is necessarily brought into contact with moisture, it is likewise highly probable that it then combines with the elements of water, forming the true ozone HO_3, and that to this the odour and oxidising actions are really due.

Ozone, formed by the slow oxidation of phosphorus in the air, exhibits the same characters as that which is obtained by electrolysis of water, &c. Ozone thus produced is generally regarded as merely allotropic oxygen; but as water is always present in its formation, it may also be a peroxide of hydrogen, like the ozone obtained from electrical sources.*

According to Schönbein, many other substances besides phosphorus possess the power of inducing the formation of ozone. Thus, ether, oil of turpentine, oil of lemons, linseed oil, alcohol, wood-spirit, various vegetable acids, sulphuretted hydrogen, arseniuretted hydrogen, and sulphurous acid, in contact with air or oxygen gas, and under the influence of light, acquire the power of decolorising indigo, and producing various oxidising actions. A similar influence is exerted by mercury and other noble metals in the finely divided state; and stibethyl is found to be a more powerful ozoniser than even phosphorus itself.

Houzeau has shown† that active oxygen may be obtained by the action of strong (monohydrated) sulphuric acid on peroxide of barium. The gas thus evolved has a very powerful odour, and a taste like that of the lobster; it rapidly decolorises blue litmus paper; oxidises silver; burns

* Williamson, Ann. Ch. Pharm. lxi. 32.
† Compt. rend. xl. 947.

ammonia spontaneously, transforming it into nitrate of ammonia; instantly burns phosphuretted hydrogen (the less inflammable variety, I. 451) with emission of light; decomposes hydrochloric acid, setting the chlorine free; is a powerful oxidising and chlorinising agent; is stable at ordinary temperatures, but loses its peculiar properties when heated to 75° C. In all these respects, it differs essentially from ordinary oxygen; in fact it exhibits the properties of ozone. Active oxygen may also be obtained from other bodies besides the peroxide of barium. Oxygen in the combined state appears, indeed, to possess the intensified power which distinguishes free oxygen in the nascent state.

The nature of ozone has also been investigated by Dr. Andrews*, who has arrived at the conclusion that electrolytic ozone, as well as that obtained from other sources, is nothing but active oxygen. The excess of the weight of ozone in Baumert's experiments, over that of the active oxygen, is attributed by Andrews to the presence of a small quantity of carbonic acid, which he states is always mixed with the gases resulting from the decomposition of water, unless especial precautions be taken to get rid of it, and being absorbed by the potash resulting from the decomposition of the neutral solution of iodide of potassium, increases the weight of the apparatus, and consequently produces an apparent increase in the quantity of ozone absorbed.

To obviate this supposed source of inaccuracy, Andrews, using an apparatus similar to that of Baumert, acidulated his solution of iodide of potassium with hydrochloric acid; and, in five experiments, in which 29 litres of the ozoniferous gas were passed through the apparatus, obtained an increase of weight in the absorption-bulbs, that is to say, a quantity of ozone — amounting to 0·1179 grm., while the quantity of active oxygen, estimated according to the quantity of iodine

* Chem. Soc. Qu. J. ix. 168.

separated, was 0·1178 grm. From this result, Andrews concludes that ozone is nothing but an active form of oxygen.

In another series of experiments, in which electrolytic ozone was decomposed by heat, and the gas subsequently passed over strong oil of vitriol and anhydrous phosphoric acid, not a trace of water could be discovered. Andrews has likewise confirmed the result obtained by other experimenters that pure dry oxygen acquires peculiar active properties by the action of the electric spark; and by comparing the properties of ozone obtained from various sources, he concludes that ozone, in whatever manner produced, is essentially the same, consisting in fact of allotropic oxygen.

On the other hand, Baumert* denies the existence of carbonic acid in the ozoniferous gas which he obtained by electrolysis, inasmuch as the electrolyte used, water acidulated with sulphuric and chromic acid, could scarcely absorb a sufficient quantity of carbonic acid to account for the results obtained. He moreover attributes the carbonic acid which Andrews obtained, to the oxidising action of the ozone on the diaphragm of bladder with which the positive cell of the decomposing apparatus was closed. Baumert finds, indeed, that when a diaphragm of bladder is used for this purpose, carbonic acid is actually produced; but when a diaphragm of gypsum is employed, not a trace of that gas can be detected. With respect to the use of iodide of potassium acidulated with hydrochloric acid, Baumert calls attention to the fact that such a solution must contain free hydriodic acid, which is decomposed by oxygen in its ordinary as well as in its allotropic state. In fact, oxygen gas evolved by electrolysis, and completely freed from ozone by passing through a neutral solution of iodide of potassium, liberated, when subsequently passed through a solution of the same salt acidulated with hydrochloric acid, a quantity of iodine much larger than that which it had previously separated from the neutral

* Pogg. Ann. xcix. 88.

solution. This may account for the greater proportion of the active oxygen to the total quantity of ozone obtained in the experiments of Andrews.

The true nature of ozone must then still be considered a matter for investigation. The existence of an allotropic modification of oxygen possessing peculiarly active properties appears to be established by the researches of numerous inquirers; but on the other hand, till some more valid objection is adduced against the results obtained by Baumert and Williamson, the existence of hydrogen in the ozone obtained by electrolysis of acidulated water can scarcely be denied.

Quantitative estimation of Oxygen and Hydrogen. — The quantity of either of these gases in a gaseous mixture may be determined by mixing it with an excess of the other, and inducing combination by the electric spark, or by spongy platinum or platinised charcoal. One-third of the volume of gas which disappears is oxygen, and two-thirds hydrogen. This, of course, implies that no other gases are present capable of uniting with either oxygen or hydrogen.

The amount of hydrogen in solid or liquid compounds (generally organic), when it is not present in the form of water, is estimated by heating the compound in contact with some oxidising agent, generally oxide of copper, and weighing the water produced (p. 662). Oxygen in such compounds is generally determined by loss, the quantities of all the other elements being determined by the methods severally applicable to them, and the remainder being estimated as oxygen. The quantity of oxygen in metallic oxides which are not reduced by heat alone, is generally estimated by igniting them in a current of hydrogen and weighing the water produced.

The quantity of oxygen in the atmosphere may be determined by methods already described (I. 331). A very good method has since been given by Liebig*, viz. to absorb the

* Chem. Soc. Qu. J. iv. 221.

oxygen by means of an alkaline solution of pyrogallate of potash. Pyrogallic acid is readily obtained as a crystalline sublimate by the dry distillation of gallic acid; it dissolves easily in potash: and the solution introduced by means of a pipette into air standing over mercury, absorbs the oxygen quickly and completely.

Estimation of Water.—The quantity of water in a solid compound, a salt for example, is determined by heating a weighed quantity of the substance in a capsule or crucible over a lamp, or in a sand-bath, or over a water-bath, according to the temperature which it will bear without giving off anything but water. Substances which will not bear even the temperature of the water-bath, are dehydrated by placing them over strong sulphuric acid, sometimes in vacuo, sometimes by merely placing the dish containing the sulphuric acid, with the substance supported above it in a capsule, on a ground glass plate, and covering the whole with a bell jar, Another method of drying substances which will not bear much heat, is to place them in a bent tube immersed in a water-bath at a regulated temperature, and pass through the tube a current of dry air, hydrogen, or carbonic acid, according to the nature of the substance.

Some salts when heated give off a portion of their acid as well as their water, the sulphates of alumina, and sesquioxide of iron for example. To determine the quantity of water in such cases, the salt must be mixed with a weighed quantity of protoxide of lead, sufficient to cover it completely, and heated in a platinum crucible: the acid, which would otherwise escape, is then retained by the oxide of lead, and nothing but water goes off.

The quantity of combined water in a base, such as hydrate of potash, is determined by heating the base with an acid which will form with it a compound not decomposable at a red heat.

In all cases, the water, instead of being estimated merely by loss of weight, may be determined by receiving it in a tube filled with dry chloride of calcium, or with pumice

stone soaked in strong sulphuric acid, an empty glass bulb, previously weighed, being, however, interposed when the quantity of water is large (Vol. I. p. 313, fig. 102). This method is particularly applicable when other substances besides water are given off at the same time.

The methods of determining the quantity of water in solutions are similar to those above described for solids (I. 545).

Absorption of gases by water and other liquids.—The laws relating to the absorption of gases by liquids have lately been examined with great care by Bunsen, whose results tend partly to confirm, partly to modify those of the older experiments of Dalton, Henry, and Saussure (I. 75, 316).

The absorption of the more soluble gases, such as ammonia, sulphurous acid, &c., was estimated by saturating the liquid with the gas at a known temperature, and then determining, either by volumetric, or by weighed analyses, the quantity of gas dissolved in a given volume of the liquid; for example, hydrosulphuric acid was precipitated by a solution of copper, sulphurous acid and chlorine were determined by the iodometric method, to be afterwards described.

For the less soluble gases, a different method was adopted. The apparatus used for the purpose, called an *absorptiometer*, consists of a graduated tube closed at the top, and containing mercury. The gas is first introduced into this tube above the mercury, and afterwards the absorbing liquid. This tube is enclosed within a wider one, the space between the two being filled with water, by means of which any required temperature may be imparted to the contents of the inner tube. The outer tube is closed at top with a lid, in the middle of which is an elastic cushion pressing firmly on the inner tube containing the gas. This tube, by a peculiar contrivance, may be either firmly closed at the bottom, or made to communicate with the mercury in the cistern in which it stands. The tubes being filled and firmly closed top and bottom, the

whole is vigorously shaken for about a minute, to bring the gas well in contact with the liquid. The inner tube is then loosened at the bottom, so as to open a communication with the mercury in the cistern, and equalise the pressure. More gas is then introduced, and the shaking repeated, and these operations are continued, till the mercury in the inner tube no longer exhibits any alteration of level. The volume of the remaining gas is then read off, and observations made of the pressure and temperature.

The volume of a gas, reduced to 0° C., and 760 mm. pressure, which is absorbed by the unit of volume of any liquid, is called the *coefficient of absorption.* The formula used by Bunsen for calculating these coefficients is founded on the law of gas-absorption discovered by Dr. Henry, viz. that at any given temperature, the weight of a gas absorbed by a given quantity of a liquid is proportional to the pressure; or, in other words, that the volume of the gas absorbed at any given temperature is the same under all pressures (I. 75). Bunsen finds, indeed, that the coefficient of absorption of any gas thus determined under different pressures, exhibits a constant value, a result which affords a striking confirmation of the truth of Henry's law.

If V and V' denote the volumes of a gas reduced to 0°, before and after absorption, P and P' the corresponding pressures, the quantity of gas absorbed under the pressure P' is $\frac{V\ P}{0{\cdot}760} - \frac{V'\ P'}{0{\cdot}760}$. To reduce this to the normal pressure, 0·760 mm., it must be multiplied by $\frac{0{\cdot}760}{P'}$; and if the volume of the absorbing liquid is h, the coefficient of absorption α, or the quantity of gas absorbed by a unit volume of the liquid, will be

$$\alpha = \frac{1}{h}\left\{ \frac{V\ P}{P'} - V' \right\}$$

The following table exhibits the coefficients of absorption of certain gases by water and alcohol for every 5 degrees centigrade of temperature:—

	Oxygen.		Hydrogen.		Nitrogen.		Nitrous Oxide.	
	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.
0° C.	0·04114			0·06925	0·02035	0·12634	1·3052	4·1780
5	0·03628			0·06853	0·01794	0·12440	1·0954	3·8442
10	0·03250	0·28397	0·0193	0·06786	0·01607	0·12276	0·9196	3·5408
15	0·02989			0·06725	0·01478	0·12142	0·7778	3·2678
20	0·02838			0·06668	0·01403	0·12038	0·6700	3·0253
25	?			0·06616	. .	0·11964	0·5962	2·8133

	Carbonic Oxide.		Carbonic Acid.		Marsh Gas.		Olefiant Gas.	
	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.
0° C.	0·03287		1·7967	4·3295	0·05449	0·52259	0·2563	3·5950
5	0·02920		1·4497	3·8908	0·04885	0·50861	0·2153	3·3234
10	0·02635	0·20443	1·1847	3·5140	0·04372	0·49535	0·1837	3·0859
15	0·02432		1·0020	3·1993	0·03909	0·48280	0·1615	2·8825
20	0·02312		0·9014	2·9465	0·03499	0·47096	0·1488	2·7131
25	. .		. .	2·7558	. .	0·45982	. .	2·5778

	Sulphurous Acid.		Hydrosulphuric Acid.		Chlorine.	Nitric Oxide.	Ammonia.
	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.	In Alcohol.	In Water.
0° C.	79·789	327·80	4·3706	17·891	. .	0·31606	1049·60
5	67·485	251·24	3·9652	14·776	. .	0·29985	917·90
10	56·647	190·02	3·5858	11·992	2·5852	0·28609	812·76
15	47 276	144·13	3·2326	9·539	2·3681	0·27478	727·22
20	39·374	113·56	2·9053	7·415	2·1565	0·26592	653·99
25	32·786	98·33	2·6041	5·623	1·9504	0·25951	585·94
30	27·161	. .	2·3290	. .	1 7499		
35	22·489	. .	2·0799	. .	1·5550		
40	18 766	. .	1·8569	. .	1·3655		

When a liquid is in contact with a mixture of several gases, with none of which it is disposed to form a definite compound, it absorbs of each gas a quantity corresponding to the pressure which this same gas exerts in the mixture that remains after the absorption is complete. Now, in any mixture of gases, each gas exerts the same pressure that it would if it alone filled the entire space; and the pressure of the entire mixture

is equal to the sum of the pressures of the separate constituents. If, for example, atmospheric air, which in 100 volumes contains 20·9 vols. oxygen, and 79·1 vols. nitrogen, exerts altogether a pressure equal to that of 760 mm. of mercury, the pressure of the oxygen is equal to $\frac{20 \cdot 9}{100} \cdot 760 = 158 \cdot 8$ mm. and that of the nitrogen is $\frac{79 \cdot 1}{100} \cdot 760 = 601 \cdot 2$ mm.

When water is saturated with atmospheric air, it takes up of each constituent a quantity determined by the existing temperature, and the partial pressure of each gas. For example, at 13° C., and under a pressure corresponding to 760 mm. of mercury, 1 volume of water absorbs $0 \cdot 03093 \times \frac{158 \cdot 8}{760} = 00646$ vols. of oxygen, measured at 0° C. and 760 mm.; and $0 \cdot 01530 \times \frac{601 \cdot 2}{760} = 0 \cdot 01210$ vols. nitrogen, also measured at the standard pressure and temperature. Hence, at 13° C. and 760 mm., 1 vol. water absorbs 0·00646 vols. oxygen, and 0·01210 vols. nitrogen, making together 0·01856 vols. of a gaseous mixture, containing 34·8 vols. oxygen, and 65·2 vols. nitrogen. Direct analysis of a gaseous mixture evolved by boiling, from water previously saturated with atmospheric air, gave 34·73 vols. pure oxygen and 65·27 vols. nitrogen.

When water previously saturated with oxygen or nitrogen is exposed to the air, the final result is still the same, the excess of either gas being given off, and the oxygen and nitrogen being ultimately absorbed in the proportions just given. If water containing any other gas is exposed to the air, the whole of the dissolved gas is ultimately eliminated, and the water becomes saturated with the atmospheric gases, in the same proportion as if no other gas had been previously dissolved in it. An exception, however, occurs when the dissolved gas is capable of forming a definite compound with

the water, in which case portions of the gas and the water evaporate together.

The general law above stated with regard to the absorption of gaseous mixtures is found to hold good in mixtures of sulphurous acid gas with hydrogen and carbonic acid; of carbonic oxide and carbonic acid; and of carbonic oxide, marsh-gas, and hydrogen; but not with a mixture of equal volumes of chlorine and hydrogen, or of chlorine with twice or four times its volume of carbonic acid.

NITROGEN.

Preparation of Nitrogen gas (I. 323).—This gas may be obtained in great abundance, and perfectly pure, by heating a solution of nitrite of potash with sal-ammoniac:

$$KO \cdot NO_3 + NH_4Cl = KCl + 4HO + 2N.$$

The solution of nitrite of potash is prepared by passing the nitrous gas, evolved by heating 1 part of starch with 10 parts of nitric acid, into a solution of caustic potash of sp. gr. 1·38, till the liquid becomes decidedly acid, and then adding a sufficient quantity of caustic potash to restore the alkaline reaction. The solution of nitrite of potash thus obtained may be preserved without alteration. On mixing this liquid with three times its bulk of concentrated solution of sal-ammoniac, and heating the mixture in a flask, nitrogen gas is given off in large quantity and with perfect regularity. Pure nitrogen may also be obtained by heating a solution of nitrite of ammonia; but this salt is difficult to prepare (Corenwinder.*)

Another method of obtaining nitrogen, mixed however with chlorine, is to heat a mixture of nitrate of ammonia and sal-ammoniac:—

$$2(NH_4 \cdot NO_6) + NH_4Cl = 5N + Cl + 12HO.$$

After the mixture has been heated to the melting point of the

* Ann. Ch. Phys. [3], xxvi. 296.

nitrate, the reaction goes on by itself. The chlorine may be afterwards absorbed by potash. (Maumené.*)

Nitrous oxide (I. 340).—This gas may be obtained in a state of purity by the action of protochloride of tin on aqua-regia. The tin-salt is dissolved in hydrochloric acid, the solution heated over the water-bath, and crystals or cylindrical lumps of nitre, successively dropped into it through a wide tube dipping into the liquid. (Gay-Lussac.†)

Nitric oxide may be obtained by a process similar to that above described for the preparation of nitrous oxide, using however protochloride of iron instead of protochloride of tin. (Pelouze and Gay-Lussac.‡)

Anhydrous nitric acid, NO_5, is obtained by the action of dry chlorine on nitrate of silver. Chlorine gas contained in a gasometer standing in sulphuric acid, is made to pass very slowly, first over chloride of calcium, then over sulphuric acid, and lastly over thoroughly dried nitrate of silver, which is heated, first to 95° C., and afterwards constantly to 58° or 60°C. The products of decomposition pass into a U-tube cooled to 21° C., in which a very volatile liquid (probably nitrous acid) collects, together with crystals of anhydrous nitric acid, while oxygen escapes. The different parts of the apparatus must be connected by fusion, as the acid vapours would quickly corrode caoutchouc joints. The anhydrous nitric acid crystallises in colourless rhombic prisms, having angles of about 60° and 120°, and in hexagonal prisms derived therefrom. It melts at 29° to 30° C., and boils at 45° to 50°C., but begins to decompose near its boiling point. It becomes strongly heated by contact with water, in which it

* Compt. rend. xxxiii. 401.

† Ann. Ch. Phys. [3], xxiii. 229.

‡ Ann. Ch. Phys. [3], 216.

dissolves without colouring or evolution of gas, forming hydrated nitric acid (H. Deville).* According to Dumas†, the crystals melt spontaneously when left to themselves; and on one occasion, when an attempt was made to recrystallise the fused mass by immersion in a freezing mixture, the tube was shattered with explosion.

Quantitative estimation of Nitrogen.—Nitrogen is estimated, either by collecting it as a gas in the free state and measuring its volume, or by converting it into ammonia. Most nitrogen-compounds, when strongly heated with the hydrates of the fixed alkalies, give off the whole of their nitrogen in the form of ammonia. This reaction is especially applied to the estimation of nitrogen in organic compounds, in which that element is united with carbon, hydrogen, &c. The organic compound is mixed with a large excess of soda-lime—a mixture of caustic soda and quick-lime, the latter being added to counteract the deliquescence of the hydrate of soda,—and heated to redness in a combustion-tube (I. 373), to which is attached a suitable bulb-apparatus containing hydrochloric acid. The ammonia is thereby absorbed, and is subsequently precipitated by chloride of platinum, in the manner described at page 385 of this volume. This method gives very exact results; but it is not applicable to compounds containing nitrogen in the form of nitric acid or of peroxide of nitrogen, because in such compounds the conversion of the nitrogen into ammonia by heating with caustic alkalies is never complete. For such compounds, it is better to evolve the nitrogen in the free state, and determine its quantity by measurement. This may be done either comparatively or absolutely.

For the *comparative* determination, the azotised organic compound is mixed with oxide of copper, and heated in a combustion-tube, the open end of which, to the depth of four or five inches, is filled with finely divided metallic

* Ann. Ch. Phys. [3]. xxviii. 241 † Compt. rend. xxviii. 323.

copper, obtained by reducing the oxide with hydrogen. By the oxidising action of the oxide of copper, the carbon of the organic compound is converted into carbonic acid, and the nitrogen into nitric oxide and other oxides of nitrogen, all of which are, however, completely decomposed in passing over the red-hot metallic copper, so that nothing but nitrogen and carbonic acid pass out. These gases are collected over mercury in a graduated tube, and their volume measured. The carbonic acid is then absorbed by potash, and the residual nitrogen also measured. Now the weights of equal volumes of nitrogen and carbonic acid are to one another as 14 to 22 (I. 149), that is to say, as the atomic weights of N and CO_2; and each atom of carbonic acid contains one atom of carbon. Consequently, the volumes of nitrogen and carbonic acid produced by the combustion of the organic compound, are to one another as the numbers of atoms of nitrogen and carbon. This method, of course, implies that the carbon in the organic compound has been previously determined.

For the *absolute* determination of nitrogen, the same method of combustion and collecting the gas is adopted, excepting that a longer combustion-tube is used, and a quantity of bicarbonate of soda is placed at the sealed end, sufficient to occupy about eight inches of the tube. The process is commenced by heating a portion of this bicarbonate of soda, so as to evolve carbonic acid, and sweep all the air out of the tube. The substance is then burned, and the evolved gases collected over mercury, the carbonic acid being absorbed by strong potash-ley placed at the top of the mercury; and when the combustion is ended, the remainder of the bicarbonate of soda is heated so as to evolve more carbonic acid, and drive all the remaining gases out of the tube. The volume of nitrogen collected is then read off and its weight calculated, the proper corrections being made for pressure and temperature. Dr. M. Simpson, of Dublin, has proposed certain modifications both in this and in the comparative method of estimating

nitrogen, with the view of facilitating the process and insuring greater accuracy. The principal of these attentions is the replacement of the oxide of copper by oxide of mercury, which gives up its oxygen more readily, and, therefore, insures a more complete combustion, especially when the substance is rich in carbon.*

The method of combustion with oxide of copper and decomposition of the oxides of nitrogen by metallic copper, is applicable to all nitrogen compounds whatsoever. For the analysis of *nitrates*, in which the nitrogen is already completely oxidised, the oxide of copper may be dispensed with, the salt being simply ignited in a tube, and the nitrous vapours passed over red-hot metallic copper. *Nitric acid* may also be determined by several other methods. When it exists in the free state in aqueous solution, its quantity may be determined by shaking up the liquid with carbonate of baryta, till the nitric acid is completely neutralised, then filtering, evaporating the filtrate to dryness, care being taken not to heat the residue too strongly, and weighing the dry nitrate of baryta thus obtained. Or the solution of nitrate of baryta may be decomposed by sulphuric acid, the sulphate of baryta weighed, and the equivalent quantity of nitric acid calculated therefrom. If the solution of nitric acid is very weak, it is better to use baryta-water to neutralise it; then pass carbonic acid gas through the liquid to remove any excess of baryta; filter; and treat the filtered solution of nitrate of baryta as above.

When nitric acid is combined with a base, it may be liberated by distillation with sulphuric acid (I. 346), and the distillate treated with carbonate of baryta or baryta-water, in the manner already described. Or a weighed portion of the nitrate may be decomposed by sulphuric acid in a platinum crucible, the residual sulphate ignited and weighed, and the quantity of nitric acid thence determined by calculation.

* Chem. Soc. Qu. J. vi. 289.

This method, however, is applicable only when the sulphate thus formed can bear a red-heat without decomposition.

For the estimation of small quantities of nitric acid, such as exist in plants, soils, and waters, some very ingenious methods have been invented by M. G. Ville.* The nitric acid is first converted into binoxide of nitrogen by boiling the solution of the nitrate with protochloride of iron and free hydrochloric acid:

$$NO_5 + 6FeCl + 3HCl = NO_2 + 3Fe_2Cl_3 + 3HO;$$

and the nitric oxide then converted into ammonia, either by passing it, mixed with excess of hydrogen, over spongy platinum heated nearly to redness:

$$NO_2 + 5H = NH_3 + 2HO;$$

or by passing it, mixed with excess of hydrogen and hydrosulphuric acid, over soda-lime heated nearly to redness:

$$NO_2 + 3HS + 2CaO = NH_3 + CaO \,.\, SO_3 + CaS_2.$$

The second method is generally the more exact of the two, the first giving accurate results only when the quantity of nitrogen to be determined is very small. The ammonia is absorbed by an acid of known strength contained in a bulb-apparatus, and its quantity determined by the alkalimetric method (I. 547); or it may be absorbed by hydrochloric acid, and precipitated by chloride of platinum. Another method is to pass the nitric oxide over red-hot metallic copper; but this method is not so exact as the preceding. To apply these methods to the determination of the quantity of nitrates in vegetable substances, soils, waters, &c., the substance (10 to 100 grammes) is exhausted with boiling water, and the concentrated solution treated as above.

Professor Way has also devised a method of estimating small quantities of nitric acid, especially adapted to rain-

* Ann. Ch. Phys. [3], vi. 20.

water and other waters. This process, which is a modification of Bunsen's volumetric method, consists in heating the solid residue obtained by evaporating about a pint of the water — previously rendered alkaline by lime-water to prevent loss of nitric acid — with hydrochloric acid and iodide of silver, in an apparatus from which the air has been completely excluded by a stream of carbonic acid gas, and exhaustion with the air-pump. The nitrates and the hydrochloric acid then decompose each other, with separation of nitric oxide and chlorine; and the chlorine decomposes the iodide of silver, liberating iodine, the amount of which is afterwards determined by a standard solution of sulphurous acid in the manner to be hereafter described. Organic matter, if present in the water, must be destroyed by adding a small quantity of permanganate of potash, during the concentration of the liquid.

The determination of the quantity of nitric acid in *nitrate of potash* is a process of considerable commercial importance, and several methods have been devised for it. Of these, however, there are only two in general use. The first, originally introduced by Gossart and improved by Pelouze, consists in boiling the acidified solution of the nitre with a solution of protochloride of iron of known strength, whereby the protoxide of iron is converted into sesquioxide, and binoxide of nitrogen is evolved, and afterwards determining the unoxidised portion of the iron by the method of Margueritte, with a standard solution of permanganate of potash (II. 56). According to Messrs. Abel and Bloxam*, this method does not always give exact results, because a portion of the nitre does not contribute to the oxidising action, either from not being completely decomposed, or from losing a portion of its acid before it comes in contact with the iron-salt. The other method, introduced by Gay-Lussac, consists in deflagrating the nitre with one fourth of its weight of finely divided charcoal (lamp-black) and 6 parts of common salt,

* Chem. Soc. Qu. J. ix. 97; x. 107.

the latter being added merely to moderate the action. The nitrate of potash is then converted into carbonate, the quantity of which in the ignited residue may be determined by the process of alkalimetry (I. 347). This method is also variable in its results, partly because a portion of the nitre is apt to escape decomposition, partly because cyanate of potash is formed during the reaction, and, when subsequently dissolved in water, is decomposed, with formation of carbonate of ammonia and carbonate of potash:

$$C_2NKO_2 + 4HO = KO.CO_2 + NH_4O.CO_2.$$

Hence, the quantity of alkali to be neutralised by the acid is greater than it should be. The presence of alkaline sulphates in the nitre also introduces an error, because these salts are reduced by ignition with charcoal to sulphides, which have an alkaline reaction. Messrs. Abel and Bloxam find that these several sources of error may be eliminated, and exact results obtained, by using the charcoal in a very finely divided state, and subsequently heating the ignited mass with chlorate of potash, which completely decomposes the cyanates and reconverts the sulphides into sulphates. The best form of carbon for the purpose was found to be the pure finely divided graphite prepared by Mr. Brodie's process (p. 661).

CARBON.

Volatility of carbon. — According to Despretz, charcoal exposed in vacuo to the heat produced by a Bunsen's battery of 500 or 600 pairs, disposed in 5 or 6 series, so as to form 100 pairs of 5 or 6 times the ordinary size, is volatilised, and collects on the sides of the vessel in the form of a black crystalline powder; in a space filled with a gas with which the carbon does not combine, volatilisation likewise takes place, but more slowly. At the same temperature, charcoal may also be bent, welded, and fused, every kind of charcoal when thus treated becoming softer the longer the heat is con-

tinued, and being ultimately converted into graphite. Diamond exposed to the same temperature is likewise converted into graphite.*

Charcoal as a disinfectant.—The power which wood-charcoal possesses of absorbing and decomposing gaseous bodies has lately been applied by Dr. Stenhouse to the construction of ventilators and respirators for purifying infected atmospheres. In a pamphlet, bearing the title "On Charcoal as a Disinfectant," Dr. Stenhouse observes — "Charcoal not only absorbs effluvia and gaseous bodies, but, especially, when in contact with atmospheric air, rapidly oxidises and destroys many of the easily alterable ones, by resolving them into the simplest combinations they are capable of forming, which are chiefly water and carbonic acid. . . . . Effluvia and miasmata are generally regarded as highly organised, nitrogenous, easily alterable bodies. When these are absorbed by charcoal, they come in contact with highly condensed oxygen gas, which exists within the pores of all charcoal which has been exposed to the air, even for a few minutes; in this way they are oxidised and destroyed." On this principle, Dr. Stenhouse has constructed *ventilators*, consisting of a layer of charcoal enclosed between two sheets of wire gauze, to purify the foul air which accumulates in water-closets, the wards of hospitals, and in the back courts and lanes of large cities. By the use of these ventilators, pure air may be obtained from exceedingly impure sources, the impurities being absorbed and retained by the charcoal, while a current of pure air alone is admitted into the neighbouring apartments. A similar contrivance might also be applied to the gully-holes of our common sewers, and to the sinks in private houses. Dr. Stenhouse has also constructed *respirators*, consisting of a layer of charcoal a quarter of an inch thick, interposed between two sheets of silvered wire gauze, covered with woollen cloth. They are made either to cover the mouth

* Compt. rend. xxviii. 755.

and nose, or the mouth alone; the former kind of respirator affords an effectual protection against malaria and the deleterious gases which accumulate in chemical works, common sewers, &c. The latter will answer the same purpose when the atmosphere is not very impure, provided the simple precaution be taken of inspiring the air by the mouth, and expiring by the nose. This form of respirator may also be useful to persons affected with fetid breath. Freshly heated wood-charcoal simply placed in a thin layer in trays, and disposed about infected apartments, such as the wards of hospitals, is also highly efficacious in absorbing the noxious matter.

Platinised charcoal. — The power of charcoal in inducing chemical combination is greatly increased by combination with minutely divided platinum. In this manner, a combination may be produced possessing the absorbent power of charcoal (which is much greater than that of spongy platinum), and nearly equal, as a promoter of chemical combination, to spongy platinum itself. In order to platinise charcoal, nothing more is necessary than to boil it, either in coarse powder or in large pieces, in a solution of bichloride of platinum, and, when thoroughly impregnated, which seldom requires more than ten minutes or a quarter of an hour, to heat it to redness in a close vessel, a capacious platinum crucible being well adapted for the purpose. Charcoal thus platinised, and containing 3 grains of platinum in 50 grains of charcoal, causes oxygen and hydrogen gases to unite completely in a few minutes; with a larger proportion of platinum, the gases combine with explosive violence, just as if platinum-black were used. Cold platinised charcoal, held in a jet of hydrogen, speedily becomes incandescent, and inflames the gas. Platinised charcoal, slightly warmed, rapidly becomes incandescent in a current of coal gas; but does not inflame the gas, owing to the very high temperature required for that purpose. In the vapour of alcohol or wood-spirit, platinised charcoal

becomes red-hot, and continues so till the supply of vapour is exhausted. Spirit of wine, in contact with platinised charcoal and air, is converted in a few hours into vinegar. Two per cent. of platinum is sufficient to platinise charcoal for most purposes. Charcoal containing this amount of platinum causes oxygen and hydrogen to combine perfectly in about a quarter of an hour, and such is the strength of platinised charcoal which seems best adapted for disinfectant respirators. Charcoal containing only one per cent. of platinum causes oxygen and hydrogen to combine in about two hours; and charcoal containing the extremely small amount of $\frac{1}{4}$ per cent. of platinum produces the same effect in six or eight hours. Platinised charcoal seems likely to admit of various useful applications; one of the most obvious of these is its excellent adaptability to air-filters and respirators. From its powerful oxidising properties, it may also prove a highly useful application to malignant ulcers and similar sores, on which it will act as a mild but effective caustic. It will probably also be found very useful in Bunsen's carbon battery (Stenhouse*).

Graphite.—This substance may be obtained in the pure and finely divided state by mixing it in coarse powder with $\frac{1}{14}$th of its weight of chlorate of potash, adding the mixture to a quantity of strong sulphuric acid equal to twice the weight of the graphite; heating the mixture in the water-bath as long as vapours of peroxide of chlorine are emitted; washing the cooled mass with water, and igniting the dry residue: it then swells up and leaves finely divided graphite. A chemical compound of sulphuric acid with a peculiar oxide of carbon appears to be formed during the process. If the graphite to be purified contains silicious matters, a small quantity of fluoride of sodium must be added to the mixture before heating (Brodie†).

* Chem. Soc. Qu. J. viii. 105.
† Ann. Ch. Phys. [3], xlv. 351.

Carbonic oxide.—This gas is rapidly absorbed by a solution of subchloride of copper in hydrochloric acid or ammonia, and indeed by the ammoniacal solutions of cuprous salts in general, *e.g.* the sulphite. A definite compound is probably formed, containing copper and carbonic oxide in equal numbers of atoms, but no such compound has yet been isolated. Ferrous and stannous salts have no action on carbonic oxide (Leblanc*).

Preparation of olefiant gas (I. 385).—The frothing which causes so much inconvenience in the preparation of this gas by the action of sulphuric acid upon alcohol, may be completely prevented by adding a sufficient quantity of sand to convert the mixture into a thick, scarcely fluid mass. The decomposition may then be carried to the end without any frothing, and nearly all the carbon of the alcohol is obtained in the form of olefiant gas. Fifty grammes of alcohol of the strength of 80 per cent. yield by this process more than 22 litres of gas (Wöhler†).

Quantitative estimation of Carbon and its compounds.—The greater number of carbon-compounds are of organic nature, and contain hydrogen as well as carbon. Hence these two elements are generally estimated together, the process consisting in burning the compound with a large excess of oxide of copper, whereby the carbon is converted into carbonic acid, and the hydrogen into water. The carbonic acid is absorbed in a weighed apparatus containing caustic potash, and the excess of weight after the absorption, gives the quantity of carbonic acid produced by the combustion, $\frac{3}{11}$ of which is the weight of the carbon. The water is absorbed in a weighed apparatus containing dry chloride of calcium, and $\frac{1}{9}$ of its weight gives that of the hydrogen. The apparatus used for the analysis is described and delineated at page 373, Vol. I. For compounds which, like oxalic acid and sugar, are easily burned, the process of heating with oxide of copper affords a

* Compt. rend. xxx. 48. † Ann. Pharm. xci. 127.

complete combustion of the carbon, and gives exact results; but when the proportion of carbon is very large, especially in fatty substances, which are not easy to burn, a different method must be adopted. Such bodies are either burned with chromate of lead, which at a red heat gives off free oxygen; or they are burned with oxide of copper, and towards the end of the process, a stream of oxygen is passed through the tube, either by placing at the closed extremity a quantity of perfectly dry chlorate of potash, and heating this salt, when the combustion of the organic substance by the oxide of copper appears to be nearly ended,—or better, by leaving that end of the tube open and connecting it with a gas-holder containing oxygen.* In this manner, the last traces of carbon are effectually burned.

The quantity of *carbonic acid* in a carbonate may be easily determined by decomposing the carbonate with sulphuric or hydrochloric acid in the apparatus represented at page 16 of this volume, the flask being weighed before and after the decomposition, and the quantity of carbonic acid estimated by the decrease of weight resulting from its evolution.

The quantity of carbonic acid contained in an aqueous solution, a mineral water for instance, may also be determined by mixing the solution with chloride of calcium and excess of ammonia and leaving it for a day in a corked flask. The precipitated carbonate of lime is then collected on a filter, washed, dried, and weighed.

The amount of carbonic acid in a gaseous mixture not containing any other acid, is estimated by absorbing the carbonic acid with caustic potash. When the proportion of carbonic acid in the mixture is considerable, this end may be attained by placing the gaseous mixture in a graduated tube over

* For details of the apparatus, and the mode of proceeding, see H. Rose (*Handb. d. Analyt. Chem.* ii. 956), and Gerhardt (*Traité de Chimie Organique*, i. 35). A very convenient apparatus for the purpose has lately been introduced by Dr. Hofmann.

mercury and passing up into it a small coke ball containing a strong solution of caustic potash; but when the proportion is very small, as in the air, this method is not sufficiently delicate. Accurate results may, however, be obtained by drawing a considerable quantity of air, by means of an aspirator, through a series of potash-bulbs (I. 373) previously weighed, the quantity of air drawn through being of course carefully measured. Another method has recently been proposed by Dr. Pettenkofer; it consists in shaking up a quantity of the air in a closed vessel of known capacity, with an excess of lime-water of known strength, and then determining the quantity of lime remaining uncombined by means of a standard solution of oxalic acid. This method is very easy of execution, and gives the means of quickly determining the varying amount of carbonic acid in the several parts of an inhabited apartment at different times.

Carbonic oxide is most readily estimated and removed from a gaseous mixture by means of a solution of dichloride of copper (p. 97) in hydrochloric acid, which absorbs it as quickly and completely as potash absorbs carbonic acid. When no other gaseous compound of carbon is present, the quantity of this gas may also be determined by exploding it with oxygen, and absorbing the resulting carbonic acid by potash. For, since carbonic acid contains its own volume of oxygen, and carbonic oxide contains half its volume of oxygen, it follows, that if carbonic oxide be exploded with half its volume of oxygen, the volume of carbonic acid produced will be equal to that of the carbonic oxide consumed: hence the volume of carbonic oxide is equal to that of the gas which disappears by absorption with potash.

The quantity of *marsh gas* or *olefiant gas* in a gaseous mixture, not containing any other carbon compound, may be determined in a similar manner. Four volumes of marsh gas, C_2H_4, require for complete combustion 8 volumes of oxygen, and produce 4 volumes of carbonic acid. For the 2 atoms of carbon require 4 atoms of oxygen, to convert them into car-

bonic acid; and the 4 atoms hydrogen require 4 atoms oxygen to convert them into water; therefore, in all, 8 atoms or 8 volumes (I. 149) of oxygen: moreover, the 4 volumes of oxygen required to consume the carbon produce 4 volumes of carbonic acid; hence the volume of gas which disappears by absorption with potash is equal to the original volume of the marsh gas.

By a similar calculation, it is found that 4 volumes of olefiant gas, C_4H_4, require 12 volumes of oxygen for complete combustion, and produce 8 volumes of carbonic acid: hence the volume of olefiant gas is equal to half the volume of gas removed by potash after the explosion. Olefiant gas may also be removed from a gaseous mixture by the introduction of a coke-ball saturated with anhydrous sulphuric acid or fuming oil of vitriol (p. 564).

For the methods of analysing gaseous mixtures containing marsh gas and olefiant gas mixed with hydrogen, carbonic oxide, nitrogen, and other gases, I must refer to works in which the operations of gas-analysis are explained in detail.*

Oxalic acid is precipitated from its aqueous solution, or from solutions of the alkaline oxalates, by chloride of calcium, ammonia being added if necessary to render the solution neutral. The precipitated oxalate of lime is converted by ignition at a low red heat into carbonate, from the weight of which the quantity of oxalic acid may be calculated, each atom of carbonate of lime ($CaO \cdot CO_2$) corresponding to 1 atom of anhydrous oxalic acid, C_2O_3: —

$$\underbrace{CaO \cdot C_2O_3}_{\text{Oxalate of lime.}} = \underbrace{CaO \cdot CO_2}_{\text{Carbonate of lime.}} + CO.$$

Consequently, 50 parts of carbonate of lime give 36 parts of anhydrous oxalic acid, C_2O_3, or 45 parts of the hydrated acid, C_2HO_4. In neutralising the solution of an acid oxalate with

* Bunsen's "Gasometry," translated by Roscoe, London, 1857; and Regnault, "Cours Elémentaire de Chimie," 2me. ed. Paris, tom. iv. pp. 73–103.

ammonia, care must be taken to avoid excess of the alkali, as in that case carbonic acid will be absorbed from the air, and carbonate of lime will be precipitated as well as oxalate. It is better, however, to precipitate oxalic acid from its acid solutions with acetate of lime, as oxalate of lime is quite insoluble in acetic acid.

Oxalic acid may also be very exactly estimated by means of a solution of terchloride of gold. The gold is then reduced to the metallic state, water is decomposed, and the liberated oxygen converts the oxalic acid into carbonic acid: —

$$3C_2O_3 + AuCl_3 + 3HO = 6CO_2 + 3HCl + Au.$$

The decomposition may be performed in the flask apparatus already referred to (fig. 1, p. 16). It takes place at ordinary temperatures, but the liquid must be boiled at the end of the process to expel the last portions of carbonic acid. This method may be applied to the decomposition of all oxalates, whether soluble or insoluble in water, the insoluble oxalates being dissolved in hydrochloric acid. An excess of that acid in the concentrated state, however, greatly interferes with the action; the liquid should, therefore, be considerably diluted with water, and the action assisted by heat. The preceding equation shows that 2 atoms carbonic acid, CO_2, correspond to 1 atom of anhydrous oxalic acid, C_2O_3, or 11 parts by weight of carbonic acid to 9 parts of anhydrous oxalic acid.

Another mode of converting oxalic acid into carbonic acid, is by acting upon it, either in the free or combined state, with binoxide of manganese and sulphuric or hydrochloric acid (p. 16).

Oxalic acid, either free or combined, is resolved, by heating with an excess of strong sulphuric acid, into a mixture of equal volumes of carbonic acid and carbonic oxide. This method may also be applied to the estimation of oxalic acid, but it is not so accurate as the preceding.

Lastly, the quantity of oxalic acid in an oxalate may be estimated by burning the compound with oxide of copper (p. 662).

Estimation of Cyanogen.—The quantity of cyanogen in a soluble cyanide is easily determined by precipitation with nitrate of silver. The precipitated cyanide of silver is collected on a weighed filter and dried at 100° C. Every 134 parts of it contain 26 parts of cyanogen. Many insoluble cyanides may be decomposed by boiling with sulphuric or hydrochloric acid, hydrocyanic acid being evolved, and the metal remaining as sulphate or chloride, from the weight of which the quantity of cyanogen which has gone off may be calculated. Lastly, all cyanogen compounds whatever may be analysed by burning with oxide of copper, in the manner already described.

BORON.

This element was formerly known only in the amorphous state, in which it is obtained by the action of potassium on boracic acid or borofluoride of potassium. But Wöhler and Deville * have lately obtained it in two distinct crystalline states, in one of which it bears a close resemblance to diamond, and in the other to graphite.

The first of these crystalline forms of boron is obtained by decomposing boracic acid with aluminium at a high temperature. When 80 grammes of aluminium in thick lumps, and 100 grammes of fused or pulverised boracic acid, are heated together in a crucible lined with charcoal to about the melting point of nickel for five hours, there are found on breaking the crucible after cooling, two distinct layers, one of which is glassy, and consists of boracic acid and alumina, while the other is metallic, tumefied, has an iron-grey lustre, and consists of aluminium mixed with a considerable quantity of crystallised boron, some of the crystals being distinctly visible at the surface. The aluminium is dissolved out by strong boiling soda-ley, and the residual boron is freed from iron by digestion

* Compt. rend. xliii. 1088.

in hydrochloric acid, and from traces of silicon by a mixture of nitric and hydrofluoric acids. It is still, however, mixed with laminæ of alumina, which must be carefully picked out.

The pure product thus obtained is *diamond-boron*, mixed, however, with a small quantity of graphitoïdal boron, which latter being very light, may be removed by suspension in water. Diamond-boron forms transparent crystals, having a honey-yellow or garnet-red colour, due to the presence of small quantities of foreign substances; it has hitherto been obtained only in confused aggregates of small crystals. In lustre and refractive power, it is scarcely inferior to the diamond; and is one of the hardest bodies known, inasmuch as it scratches corundum, and even the diamond itself. It does not fuse at the heat of the oxyhydrogen blowpipe, and withstands the action of oxygen even when strongly heated; but it is slightly oxidised at the temperature at which the diamond burns, a film of boracic acid being then formed, which protects the remainder of the crystals from oxidation. Heated to redness in chlorine gas, it burns and produces chloride of boron. Heated by the blowpipe between two pieces of platinum-foil, it forms a fusible boride of platinum. It is not attacked by acids at any temperature, but when heated to redness with bisulphate of potash, it is converted into boracic acid. It is not attacked by a strong boiling solution of caustic soda; but hydrate and carbonate of soda dissolve it slowly at a red heat. Nitre does not appear to act upon it sensibly at that temperature.

Graphitoïdal Boron is produced in small quantity simultaneously with diamond-boron by the process above described. But it is obtained much more readily by treating borofluoride of potassium with aluminium, adding as a flux a mixture of equal parts of chloride of potassium and chloride of sodium; in this manner, small masses of boride of aluminium are obtained, which, when digested in hydrochloric acid, leave graphitoïdal boron. The laminæ of this substance

are often hexagonal: they have a slight reddish colour, and the form and lustre of native graphite. They are always opaque.

Amorphous boron is formed in the preparation of diamond-boron when a small globule of aluminium comes in contact with a large quantity of boracic acid, so that the boron does not dissolve in the aluminium as fast as it is set free. In this case, after the aluminium has been removed by the use of caustic soda and hydrochloric acid, the boron remains as an amorphous mass of a light chocolate colour, and exhibiting the properties which have long been known as belonging to boron. When the amorphous boron is collected on a filter, the portion which remains adhering to the filter, burns, when the paper is dried and set on fire, very easily and with an intense light; graphitoïdal boron, under the same circumstances, does not burn at all.

Boracic acid.—According to A. Vogel *, the brown colour imparted to turmeric by boracic acid is distinguished from that produced by alkalies, by not being destroyed by the action of acids. Thus, when an alcoholic tincture of turmeric diluted with water till its colour becomes light yellow, is added to a concentrated solution of borax, the yellow colour is changed to brown by the alkaline reaction of the salt, but on adding a certain quantity of sulphuric acid, the yellow colour is restored. A larger quantity of sulphuric acid sets free the boracic acid, and again produces a brown colour; which, however, does not disappear on further addition of the acid.

For detecting small quantities of boracic acid in solutions, mineral waters, for instance, H. Rose † acidulates the liquid with hydrochloric acid, dips a strip of turmeric paper into the liquid, and then leaves it to dry; if boracic acid is present, the part of the paper which has been immersed in the liquid, assumes a red-brown colour.

* Repert. Pharm. iii. 178.

† Handb. d. Analyt. Chem. i. 919, 946.

Boracic acid being but a weak acid, its salts are often decomposed by water. A concentrated solution of borax, added to nitrate of silver, throws down white borate of silver; but a dilute solution — which in fact consists of borate of water mixed with free soda — forms a brown precipitate of oxide of silver. If to a strong solution of borax, an alcoholic tincture of litmus reddened by acetic acid be added in such quantity that the red colour is nearly but not quite destroyed, and the liquid be then diluted with water, the red colour is immediately changed to blue (H. Rose*).

Nitride of Boron, BN.—This compound was discovered by Balmain †, who at first regarded it as capable of uniting with metals and forming compounds analogous to the cyanides, but afterwards found that all these supposed metallic compounds were one and the same substance, viz. nitride of boron, without any appreciable amount of metal. Balmain obtained this substance by heating boracic acid with cyanide of potassium or cyanide of zinc, or with cyanide of mercury and sulphur. It has since been more completely investigated by Wöhler ‡, who prepares it by heating to bright redness, in a porcelain or platinum crucible, a mixture of 2 pts. of dried sal-ammoniac and 1 pt. of pure anhydrous borax. The product is a white porous mass, which is pulverised and washed with water to free it from chloride of sodium. The final washings must be made with boiling-water acidulated with hydrochloric acid. Boracic acid may be used in the preparation instead of borax. Wöhler formerly obtained the nitride of boron by igniting anhydrous borax with ferrocyanide of potassium.

Nitride of boron is a white amorphous powder, tasteless, inodorous, soft to the touch, insoluble in water, infusible, and non-volatile. Heated at the point of the blowpipe-flame, it

* Ann. Ch. Pharm. lxxxiv. 216.

† Phil. Mag. [3]. xxi. 170; xxii. 467; xxiii. 71; xxiv. 191.

‡ Ann. Ch. Pharm. lxxiv. 70.

burns with a bright greenish-white flame. It easily reduces the oxides of copper and lead, giving off nitrous fumes. Heated in a current of aqueous vapour, it yields ammonia and boracid acid: —

$$BN + 3HO = BO_3 + NH_3.$$

Alkalies, and the greater number of acids, even in the state of concentrated solution, have no action on nitride of boron; strong sulphuric acid, however, with the aid of heat, ultimately converts it into ammonia and boracic acid. Fuming hydrofluoric acid converts it into borofluoride of ammonium. Nitride of boron undergoes no alteration when heated in a current of chlorine. When fused with hydrate of potash, it gives off a large quantity of ammonia. With anhydrous carbonate of potash, it yields borate and cyanate of potash: —

$$BN + 2(KO \cdot CO_2) = BO_3 \cdot KO + C_2NO \cdot KO.$$

It does not decompose carbonic acid, even at the highest temperatures. Marignac * found also that nitride of boron does not form definite compounds with metals, and that its formula is BN.

Estimation of Boron and Boracic acid. — The most exact method of estimating boron is to convert it into borofluoride of potassium, $KF \cdot BF_3$. If the substance to be treated is free boracic acid or an alkaline borate, a sufficient quantity of potash is first added, then an excess of pure hydrofluoric acid (so that the escaping vapours may redden litmus), and the mixture is evaporated to dryness in a silver or platinum vessel. The dry saline mass is then stirred up with a solution of acetate of potash containing 20 per cent. of the salt; then, after a few hours, thrown on a weighed filter, and the precipitate washed, first with the solution of acetate of potash, till the filtrate no longer gives a precipitate with chloride of calcium, then with strong alcohol, and dried at 100°.

* Ann. Ch. Pharm. lxxix. 247.

The residue consists of borofluoride of potassium, every 124·7 parts of which correspond to 34·9 of boracic acid and 10·9 of boron.

The twenty per cent. solution of acetate of potash dissolves chloride of potassium and phosphate of potash, and likewise the sulphate, though less readily; it also dissolves soda-salts; the fluoride, however, slowly. Any other bases which may be combined with the boracic acid, must be previously separated by boiling or fusing the compound with carbonate of potash (A. Stromeyer *).

Boracic acid cannot be estimated in its aqueous solution by simple evaporation to dryness, since a large quantity of it goes off with the watery vapour.

SILICON.

Silicon, like boron, may be obtained in three states analogous to the amorphous, graphitoïdal, and diamond forms of carbon. The amorphous variety is that which Berzelius obtained by the action of potassium on silicofluoride of potassium (I. 391). H. Ste-Claire Deville† prepares amorphous silicon by passing the vapour of the chloride over red-hot sodium in an atmosphere of dry hydrogen. The silicon thus obtained exhibits, after washing and drying at a moderate heat, the properties described by Berzelius.

Silicon is fusible — its melting point being intermediate between the melting points of steel and cast-iron; but when heated in the air, it quickly becomes encrusted with a coating of silicic acid, which being exceedingly difficult of fusion, causes the silicon also to appear infusible.

Graphitoïdal Silicon.—This modification of silicon was first obtained by Deville in preparing aluminium by the electro-

* Ann. Ch. Pharm. c. 82.

† Ann. Chem. Phys. [3], xlix. 62.

lysis of the double chloride of aluminium and sodium. The first portions of aluminium thus obtained are contaminated with silicon derived from the charcoal electrodes; and when this alloy of silicon and aluminium is treated with hydrochloric acid, the silicon remains undissolved in the form of shining metallic scales resembling graphite. A more productive method of obtaining this variety of silicon is given by Wöhler.* It consists in mixing aluminium with between 20 and 40 times its weight of silico-fluoride of potassium, and heating the mixture in a Hessian crucible to the melting point of silver. A metallic button is thus obtained, which, when treated successively with hydrochloric and hydrofluoric acids, yields graphitoidal silicon, partly in isolated hexagonal tables, the edges of which are often curved. This graphitoidal silicon exhibits all the properties ascribed by Berzelius to silicon which has been strongly heated. Its density is 2·49, which is less than that of quartz (from 2·6 to 2·8). It may be heated to whiteness in oxygen gas without burning or undergoing any alteration in weight; but when heated to redness with carbonate of potash, it decomposes the carbonic acid, with vivid emission of light and formation of silica. It is not attacked by any acid. A strong solution of potash or soda dissolves it slowly, with evolution of hydrogen. Heated to commencing redness in dry chlorine gas, it burns completely, and forms chloride of silicon.

Octohedral or Diamond Silicon.—When vapour of chloride of silicon is passed over aluminium kept in a state of fusion in an atmosphere of hydrogen, part of the aluminium is converted into chloride, which volatilises, and the silicon thereby separated dissolves in the remaining aluminium, which thus becomes more and more saturated with silicon; and at length a point is attained at which the excess of silicon separates from the melted aluminium in large beautiful needles, having a dark iron-grey colour, reddish by reflected light, and ex-

* Compt. rend. xlii. 48.

hibiting iridescence like that of iron-glance. These crystals are derived from the regular octohedron, and often, like the diamond, exhibit curved faces; they are very hard, and are capable of scratching and of cutting glass (Deville).

Atomic weight of Silicon.—It is still a disputed question whether the atomic weight of silicon should be 21·35 or 14·1 and accordingly, whether the formula of the oxide, chloride, &c., should be SiO_3, $SiCl_3$ &c., or SiO_2, $SiCl_2$, &c. The vapour-density of the chloride, 5·939 according to Dumas, is in favour of the formula $SiCl_2$, which gives a condensation to 2 volumes (or rather Si_2Cl_4 giving a condensation to 4 vols.), whereas the formula $SiCl_3$ would involve the very unusual condensation to 3 volumes. An argument in favour of this latter formula has been drawn from the difference between the boiling points of the bromide and chloride of silicon (153° — 59°C = 94 = 3 × 32 nearly), inasmuch as the earlier researches of H. Kopp had led him to conclude that the boiling points of analogous chlorides and bromides generally differ by multiples of 32° C. Kopp has, however, more recently shown that this law is very far from being a general expression of observed results, and that the difference, 23·5° or its multiples, occurs quite as frequently. Now the difference 94 between the boiling points of bromide and chloride of silicon, is just 4 × 23·5, and is therefore so far consistent with the formulæ Si_2Br_4 and Si_2Cl_4.

Colonel Yorke * has endeavoured to determine the formula of silicic acid, by ascertaining the quantity of carbonic acid displaced from excess of an alkaline carbonate by fusion with a given weight of silica. Experiments with carbonate of potash gave, as a mean result, 30·7 for the equivalent of silicic acid, agreeing with the formula SiO_2 (14·1 + 2 × 8 = 30·1). Experiments with carbonate of soda gave 21·3 for the equivalent of silicic acid, agreeing nearly with half that which is represented by the formula SiO_3 (21·35 +

* Proceedings of the Royal Society, viii. 140.

$3 \times 8 = 45{\cdot}35$). Experiments with carbonate of lithia gave the number 14·99, agreeing nearly with the formula SiO. By fusing 23 parts of silica with 54 parts of carbonate of soda, dissolving the fused mass in water, and evaporating the solution in vacuo, a crystallised salt was formed containing (besides 5 per cent. of carbonate of soda) the salt $NaO . SiO_2 + 7HO$. These results seem to show that silicon is capable of uniting with oxygen in more than one proportion, a conclusion in accordance with the results obtained by other experimenters.

Wöhler and Buff*, by heating silicon to low redness in a current of dry hydrochloric acid gas, have obtained a new chloride of silicon, which is a mobile fuming liquid, more volatile than the terchloride. Water decomposes this liquid, forming hydrochloric acid, and a new oxide of silicon, which is a white substance, slightly soluble in water, but dissolving very easily in alkalies,—even in ammonia, with evolution of hydrogen and formation of silicic acid. When heated in the air, it burns with a white flame. This compound is evidently a lower oxide of silicon, but its exact composition has not yet been determined.

Fuchs has obtained two hydrates of silicic acid; one containing between 9·1 and 9·6 per cent. of water, the other between 6·6 and 7 per cent. The former might be denoted by either of the formulæ, $2SiO_3 . HO$ or $3SiO_2 . HO$, according to the atomic weight of silicon chosen; but the latter agrees only with the formula, $4SiO_2 . HO$.†

The true formula of silicic acid and atomic weight of silicon must then be considered as still undecided; the balance of evidence seems, however, to incline in favour of the formula SiO_2, making the atomic weight of silicon 14·1. The analogy between silicic acid and titanic acid points to the same conclusion.

Siliciuretted Hydrogen.—A remarkable gaseous compound

* Compt. rend. xliv. 834.

† Ann. Ch. Pharm. lxxxii. 119.

of silicon and hydrogen is produced when a bar of aluminium containing silicon is connected with the *positive* pole of a Bunsen's battery of 8 to 12 cells, and made to dip into a solution of chloride of sodium. The aluminium then dissolves in the form of chloride, a considerable quantity of gas is evolved at its surface, and many of the gas-bubbles, as they escape into the air, take fire spontaneously, burning with a white light and diffusing a white fume. When the gas is collected in a tube over water, and bubbles of oxygen are passed up into it, each successive bubble produces at first a brilliant white light and a copious white fume; but this effect gradually diminishes in intensity, and at last the remaining gas will no longer burn spontaneously by contact with oxygen. This residual gas is hydrogen; the spontaneously inflammable gas, which forms but a small portion of the mixture, is siliciuretted hydrogen. When the gaseous mixture is made to escape from a glass jar provided with a stop-cock, it burns in a jet, and deposits silica round the orifice. A piece of white porcelain held in the flame, becomes stained with a brown deposit of silicon; and if the gas be made to pass through a narrow glass tube, and heated till the glass softens, a deposit of silicon is likewise obtained, and the gas which issues from the tube is no longer spontaneously inflammable. The compound has not yet been analysed quantitatively.

The formation of siliciuretted hydrogen appears to be due to a secondary action accompanying the electrolysis of the saline solution. The aluminium, forming the positive pole of the battery, combines with the chlorine and dissolves; but the quantity of aluminium removed is about one-fourth greater than that which is equivalent to the quantity of chlorine eliminated from the solution. This excess of aluminium is found to be removed in the form of alumina, uniting with oxygen derived from the water of the solution. The equivalent quantity of hydrogen is of course evolved, and part of it enters into combination with the silicon contained

in the aluminium. The compound has not yet been obtained by a purely chemical reaction; but it has been observed that the hydrogen evolved, when aluminium dissolves in hydrochloric acid, burns with a brighter flame than pure hydrogen, and yields a small deposit of silica (Wöhler and Buff*).

Estimation of Silicon and Silicic acid.—When silica exists in solution, it may be completely separated from all the other substances present, by acidulating the solution with hydrochloric acid, evaporating to dryness, and boiling the residue with water containing hydrochloric acid, which will dissolve everything excepting the silica. The residue may then be dried, ignited, and weighed. The completeness of this separation depends on the perfect drying of the silica before it is boiled with the acidulated water. Now, to ensure this complete dryness, the silica must be heated somewhat above the temperature of the water-bath, the drying being completed on a sand-bath or over a lamp. In doing this, it sometimes happens that too much heat is applied, and, in that case, certain other substances, especially alumina and oxide of iron, may also be rendered insoluble in the dilute acid. To obviate this source of error, the dried residue must be moistened all over with strong hydrochloric acid, then left to stand for half an hour, and afterwards boiled with water. Everything will then dissolve excepting the silica.

Analysis of Silicates.—Some natural silicates, cerite, for example, are completely decomposed by hydrochloric acid. In that case, it is sufficient to boil the pulverised mineral with strong hydrochloric acid as long as anything continues to be dissolved; then evaporate to complete dryness, and treat the residue as above. The liquid filtered from the insoluble silica contains the bases of the mineral, which may be separated and estimated by methods already described.

* Ann. Ch. Pharm. ciii. 218.

Silicates which, like felspar, resist the action of hydrochloric acid, are decomposed by fusion with an alkaline carbonate. The mineral, very finely powdered, is mixed in a platinum crucible with three or four times its weight of dry carbonate of soda; the platinum crucible, placed within an earthen crucible lined with magnesia, and heated to bright redness in a furnace for about twenty minutes; the fused mass, when cold, removed from the crucible by digestion in dilute hydrochloric acid with the aid of heat; the whole evaporated to dryness; and the silica separated, and the bases determined as above. Some silicates, zircon for example, resist the action of alkaline carbonates, and must be decomposed by fusion with hydrate of potash or soda in a silver crucible.

By this process, not only the silica, but all the bases of a silicate may be determined, excepting the alkalies. To determine these, the mineral, reduced to an almost impalpable powder, is very intimately mixed with five times its weight of pure carbonate of lime, and the mixture exposed in a platinum crucible, protected as above, to the strongest heat of an air-furnace for about half an hour. The mass, which is not fused, but sintered together, is then digested in dilute hydrochloric acid; the silica separated as before; the greater part of the lime and likewise the bases of the silicate precipitated by carbonate of ammonia and free ammonia; the filtrate evaporated to dryness, and the ammoniacal salts expelled by ignition; the residue redissolved in water; the remainder of the lime precipitated by oxalate of ammonia; and the ammoniacal salts again expelled by evaporation and ignition. The residue then contains nothing but the chlorides of the fixed alkalies and magnesia, if that substance was contained in the mineral. Carbonate of baryta may also be used instead of carbonate of lime, and the excess of baryta removed by sulphuric acid.

Another method of obtaining the alkalies in a silicate, is to

decompose it with hydrofluoric acid aided by a gentle heat. The acid must be added by small portions to the finely pulverised mineral contained in a platinum dish, till the action ceases and the whole is reduced to a pasty mass. This mass is then heated with strong sulphuric acid, which expels fluoride of silicon and hydrofluoric acid; the residue is heated to low redness to expel the excess of sulphuric acid; the dry mass, when cold, moistened with strong hydrochloric acid, and, after standing for about half an hour, digested with water. The whole then dissolves, provided the decomposition by the hydrofluoric acid has been complete. The solution contains the alkalies and the other bases in the state of sulphates.

SULPHUR.

Allotropic Modifications of Sulphur (I. 396).—Among the various modifications of sulphur, there are, according to Berthelot*, two principal states which are more stable than the rest, and are, in fact, the limits to which all the others may be reduced. These are, first, the *octohedral*, or *electro-negative* sulphur, which acts as a supporter of combustion, and the *electro-positive*, or combustible sulphur, which is generally amorphous and insoluble in bisulphide of carbon, alcohol, &c.

Allied to octohedral sulphur are two conditions of inferior stability, viz. the prismatic variety, which crystallises from melted sulphur, and the soft emulsionable sulphur (milk of sulphur), precipitated from the solution of an alkaline polysulphide by the action of acids. Both these varieties of sulphur are soluble in bisulphide of carbon, and change spontaneously into octohedral sulphur after a certain time.

Electro-positive sulphur, properly so called, is that which is obtained when sulphur separates from any of its compounds with oxygen, chlorine, bromine, &c., the chloride or bromide yielding the most stable variety. It is amorphous and

* Ann. Ch. Phys. [3], xlix. 430.

insoluble in solvents properly so called, that is to say, in liquids which do not act upon it chemically, such as water, alcohol, ether, bisulphide of carbon, &c.

To this electro-positive sulphur are allied several modifications more or less distinct, which may perhaps be reduced to three principal varieties, all amorphous, but less stable than the one just mentioned, viz. the soft sulphur precipitated from solutions of the hyposulphites; the insoluble sulphur obtained by exhausting flowers of sulphur with alcohol and bisulphide of carbon; and the insoluble sulphur obtained by exhausting with bisulphide of carbon the soft sulphur produced by the action of heat. These varieties are distinguished one from the other by the greater or less facility with which they are transformed into soluble crystallisable sulphur, either by a temperature of 100° C., or by contact with certain electro-positive bodies, such as the alkalies and their sulphides, an alcoholic solution of hydrosulphuric acid, &c. By the contrary influences, that is to say, by contact with bodies having a decided electro-negative character, they may all be reduced to the most stable insoluble variety, viz. that which is deposited from the chloride or bromide of sulphur.

The particular modification which sulphur assumes when separated from any of its compounds, depends essentially on the nature of that compound. It is altogether independent of the state of the sulphur previous to combination, and likewise of the reagent which produces the separation, provided that reagent has neither a decided electro-positive character, such as the alkalies, nor a decided electro-negative or oxidising character, and provided that it acts rapidly and without any considerable evolution of heat. The influence of these latter conditions, is due chiefly to the unequal stability of the several modifications of sulphur. Of all these varieties, the octohedral sulphur is the most stable, and that to which all the others, even the most electro-positive, tend to return, especially under the influence of heat. (Berthelot.)

Sulphur, deposited at the positive pole of the voltaic battery in the electrolysis of an aqueous solution of hydrosulphuric acid, is soluble in bisulphide of carbon and crystallisable; but that which is deposited at the negative pole in the electrolysis of sulphurous or sulphuric acid, is insoluble in bisulphide of carbon. (Berthelot.*)

Magnus † obtained a *black* modification of sulphur by repeatedly heating sulphur to 300° C., cooling suddenly, and exhausting with bisulphide of carbon; and this black sulphur, heated to a temperature between 130° and 150°, passed into a red modification. According to Mitscherlich, however, pure sulphur does not exhibit these modifications, but when sulphur is melted with small quantities of fatty matters, various highly coloured products are obtained. Even the grease imparted by touching sulphur with the fingers, is sufficient to alter its colour considerably when melted.

Vapour of sulphur, when it comes in contact with cold bodies, condenses in the form of *utricles*, that is to say, of globules composed of a soft external pellicle filled with liquid sulphur. They sometimes retain their liquid form for a considerable time. This utricular condition has also been observed in selenium, iodine, phosphorus, and arsenious acid. (Brame.‡)

Respecting the melting point of sulphur, the observations of different experimenters vary from 104·5° to 112·2° C. This discrepancy is attributed by Professor Brodie § to the fact that the melting point of sulphur varies according to its allotropic state. According to the observations of that chemist, rhombic or octohedral sulphur (crystallised from bisulphide of carbon, alcohol, or benzol) melts at 114·5° C.; but, between 100° and 114·5°, it is transformed into the oblique prismatic modification, which melts at 120°, and if not afterwards more strongly

* Pogg. Ann. xcii. 308.

† Ann. Ch. Pharm. ci. 58.

‡ Compt. rend. xxix. 657; xxxiii. 538. 579.

§ Proceedings of the Royal Society, vii. 24.

heated, solidifies at nearly the same point. If, however, its temperature be further raised, it does not solidify till cooled to 111·5°, and if it be then heated, melts at a point very little higher. In fact, above 120°, sulphur begins to pass into the plastic state, which is more fusible. The variety insoluble in bisulphide of carbon has a melting point considerably above 120°. The gradual loss of transparency of the prismatic sulphur crystallised from fusion, arises, according to Brodie, from the hardening of plastic sulphur mechanically enclosed within the crystals. When crystals which have thus lost their transparency, are digested in bisulphide of carbon, a portion always remains undissolved. If sulphur which has been fused and strongly heated, be suddenly cooled by a mixture of solid carbonic acid and ether, it solidifies in a hard, perfectly transparent mass, which becomes soft and elastic at ordinary temperatures. This appears, indeed, to be the solid state of plastic sulphur.

Formation of Anhydrous Sulphuric acid. — When a dry mixture of 2 vols. sulphurous acid and 1 vol. oxygen or atmospheric air, is passed through a red-hot glass tube containing certain metallic oxides, *e. g.* cupric, ferric, or chromic oxide, the gases unite and produce dense white fumes of anhydrous sulphuric acid. A mixture of the oxides of copper and chromium induces the combination with peculiar facility. These oxides appear to be capable of inducing the combination of unlimited quantities of sulphurous acid and oxygen. Spongy metallic copper produces the same effect when heated, but not till the copper has become oxidised. Clean polished platinum foil, or spongy platinum, produces the combination considerably below a red heat, but not at ordinary temperatures. (Wöhler.*)

Sulphide of Nitrogen (I. 424).—This body was discovered by Soubeiran, who assigned to it the formula NS_3; but it has

* Ann. Ch. Pharm. lxxxi. 255.

since been more minutely examined by Fordos and Gélis*, who have shown that its true formula is NS_2. The best mode of preparing it is to pass dry ammoniacal gas into a solution of protochloride of sulphur, SCl, in eight or ten times its volume of bisulphide of carbon. Crystals of sal-ammoniac are then deposited, and the solution becomes darker in colour, and deposits cochineal-coloured flakes, which soon decompose and turn brown. An excess of ammonia decomposes this brown compound. The current of gas must be continued till the solution acquires an orange-yellow colour, and contains only very slightly coloured flakes, which may be separated by filtration. The filtrate, when left to evaporate, deposits crystals of sulphur, while the sulphide of nitrogen remains in the mother liquid, and may be obtained by further evaporation of the decanted liquid. The reaction is as follows: —

$$3SCl + 4NH_3 = NS_2 + S + 3NH_4Cl.$$

At the same time, however, there are a number of intermediate products formed (the brown flocculent matters above-mentioned), consisting of compounds of sulphide of nitrogen with chloride of sulphur, viz., $SCl \,.\, NS_2$; $SCl \,.\, 2NS_2$; and $SCl \,.\, 3NS_2$; but these are all ultimately decomposed by excess of ammonia. Sulphide of nitrogen forms similar compounds with dichloride of sulphur, S_2Cl.

Sulphide of nitrogen is insoluble in water, slightly soluble in alcohol, wood-spirit, ether, and oil of turpentine; bisulphide of carbon dissolves it to the amount of 15 parts in 1000, and the solution deposits the compound in small elongated prisms derived from the right rhomboïdal prism, and terminated with dihedral summits; they are transparent and of a golden yellow colour. The solution must, however, be evaporated immediately, for it decomposes after a short time, yielding hydrosulphocyanic acid, and a yellow substance like that

* Compt. rend. xxxi. 702.

which is commonly called sulphocyanogen. Water slowly decomposes sulphide of nitrogen, yielding free ammonia, together with hyposulphurous and trithionic acids :—

$$4NS_2 + 15HO = NH_4O \,.\, S_2O_2 + 2(NH_4O \,.\, S_3O_5) + NH_3.$$

Protosulphide of Carbon, CS.—This compound is obtained: 1. By passing the vapour of bisulphide of carbon over spongy platinum or pumice-stone heated to redness; sulphur is then deposited, and the protosulphide liberated in the form of gas. 2. In the preparation of the bisulphide, and simultaneously therewith. 3. By decomposing the vapour of the bisulphide at a red heat by means of lamp-black, wood-charcoal, and especially by animal charcoal in fragments. 4. By decomposing the vapour of the bisulphide at a red heat with hydrogen. 5. By calcining sulphide of antimony with excess of charcoal. 6. By the action of carbonic oxide on hydrosulphuric acid at a red heat:—

$$CO + HS = HO + CS.$$

7. By the action of sulphurous acid, or chloride of sulphur, on olefiant gas at a red heat. 8. In the decomposition of sulphocyanogen by heat, &c.

The first process yields the gas tolerably pure; that which is obtained by the other processes is mixed with hydrosulphuric acid, and carbonic oxide. It is purified by passing it rapidly through solutions of acetate of lead, and dichloride of copper dissolved in hydrochloric acid, then dried and collected over mercury.

Protosulphide of carbon is a colourless gas, having a strongly ethereal odour, resembling that of the bisulphide, but not disagreeable. When breathed in too large a quantity, it appears to be powerfully anæsthetic. It burns with a fine flame, producing carbonic and sulphurous acids, and a little sulphur. Its density is somewhat greater than that of carbonic acid. It does not liquefy at the temperature of a mix-

ture of ice and salt. Water dissolves nearly its own volume of this gas; but decomposes it somewhat quickly into hydrosulphuric acid and carbonic oxide. It is scarcely more soluble in alcohol or ether. It is not absorbed by a solution of dichloride of copper. Acetate of lead is slowly blackened by it. It is rapidly decomposed by solutions of the caustic alkalies. With lime-water, it yields sulphide of calcium, and a volume of carbonic oxide equal to its own: —

$$CaO + CS = CaS + CO.$$

This reaction establishes its composition, which is further confirmed by the fact, that, when exploded with oxygen, it yields equal volumes of carbonic and sulphurous acids. At a red heat, it is slightly decomposed: 1. By spongy platinum; 2. By aqueous vapour, into HS and CO; 3. More readily by hydrogen into HS and a hydrocarbon; 4. Completely by copper, yielding sulphide of copper, and graphitoïdal carbon; 5. By an equal volume of chlorine in sunshine, with formation of products not yet examined. (Baudrimont.*)

Bisulphide of Carbon.—By the action of nascent hydrogen (generated by slowly decomposing hydrochloric acid with zinc) upon bisulphide of carbon, Girard† has obtained a compound, CHS, which is neutral to vegetable colours, has a powerful odour, is insoluble in water, dissolves sparingly in alcohol, ether, and rock-oil, more readily in chloroform and bisulphide of carbon, but most readily in benzol; crystallises from its solutions in square prisms; sublimes undecomposed at 150° C. in long needles; but decomposes at 200°. It is not altered by alkalies; dissolves in warm hydrochloric acid; and is decomposed by nitric and by strong sulphuric acids. It forms crystalline compounds with nitrate of silver, and with the chlorides of platinum, gold, and mercury.

Bisulphide of carbon, enclosed with water in a sealed tube,

* Compt. rend. xliv. 1000.
† Compt. rend. xliii. 396.

and heated for three or four hours to 150° C., is resolved into carbonic and hydrosulphuric acids. Many metallic oxides and salts, treated in a similar manner with bisulphide of carbon, yield carbonic acid and a metallic sulphide. (Schlagdenhauffen.*)

Quantitative estimation of Sulphur and its compounds.—Sulphur is almost always estimated in the form of sulphuric acid. To determine the quantity of sulphur in a metallic sulphide, the compound is heated with nitric acid, aqua-regia, or sometimes with a mixture of hydrochloric acid and chlorate of potash, till the metal is oxidised, and the sulphur converted into sulphuric acid. The solution is then treated with chloride of barium or nitrate of baryta, and the precipitated sulphate of baryta collected on a filter, washed, dried, and ignited. Before adding the baryta-solution, however, the liquid must be considerably diluted with water, because the nitrate and chloride of barium are themselves insoluble in strong nitric and hydrochloric acids. The liquid is then boiled, and afterwards left to stand till the precipitate has completely settled down; after which the clear liquid is first passed through the filter, and then the precipitate thrown upon it; if the precipitate be poured upon the filter before it has settled down, it will be sure to run through. As the oxidation of the sulphur is very slow, the metal being completely oxidised and dissolved long before it, and a portion of the sulphur separated in the free state, it is sometimes convenient to collect this portion on a small weighed filter, determine its amount by direct weighing, and afterwards estimate the dissolved portion as above.—In the sulphides of gold and platinum, from which the sulphur is completely expelled by ignition, its quantity may be at once determined by weighing the residual metal. The sulphides of the alkali-metals and alkaline earth-metals are sometimes

* J. Pharm. [3], xxix. 401.

analysed by decomposing them with hydrochloric acid, receiving the evolved hydrosulphuric acid in a solution of acetate of lead, oxidising the precipitated sulphide of lead with fuming nitric acid, weighing the sulphate of lead thus produced, and thence calculating the quantity of sulphur.

The sulphur in organic compounds may likewise be estimated by oxidising the compound with fuming nitric acid, and precipitating the resulting sulphuric acid with a baryta-solution. Another method, given by Dr. W. J. Russell*, is to burn the substance in a combustion-tube with oxide of mercury, carbonate of soda being added to take up the sulphuric acid produced, and a small bent tube dipping under water fitted into the open end of the combustion-tube, so that any acid vapours that escape may be condensed in the water. At the end of the combustion, this liquid is acidulated with hydrochloric acid; the tube washed out with the acid solution; the liquid filtered; and the sulphuric acid precipitated by chloride of barium.

The quantity of *sulphuric acid* in a soluble sulphate is estimated by precipitating the aqueous solution with chloride of barium. Some sulphates which are insoluble in water may be dissolved in hydrochloric or nitric acid, and the baryta-solution then added. The sulphates of lime, strontia, and lead may be decomposed by boiling with a solution of carbonate of soda (II. 598), and the sulphuric acid precipitated by chloride of barium from the filtered solution, previously acidulated with nitric or hydrochloric acid. Sulphate of baryta must be decomposed by fusion in a platinum crucible with three times their weight of carbonate of soda; the fused mass digested in water; the filtered soda-solution acidulated; and the sulphuric acid precipitated as above.

Sulphurous and hyposulphurous acid may be estimated by oxidation with nitric acid, whereby they are converted into sulphuric acid, or by Bunsen's iodometric method (p. 722).

* Chem. Soc. Qu. J. vii. 212.

SELENIUM.

Preparation of Selenium (I. 427).—This element is extracted from natural selenides, and principally from the seleniferous ores of the Harz, by the following process:—The pulverised ore is treated with hydrochloric acid, to remove the earthy carbonates with which it is mixed. The residue, after being well washed and dried, is mixed with its own weight of black flux, and calcined for an hour at a red heat. Selenide of potassium is thus formed, which is separated by washing the cooled and rapidly pulverised residue with boiling water. A brown-red solution is thus obtained, and the insoluble matter which remains on the filter retains the metals (copper, lead, and silver) which were combined with the selenium. The solution of selenide of potassium oxidises gradually on exposure to the air, potash being formed, and the selenium collecting in a grey mass, which is carefully washed, dried, and distilled.

When the selenium contains sulphur, it is converted into seleniate and sulphate of potash by calcination with a mixture of nitre and carbonate of potash. The calcined mass is dissolved in hydrochloric acid, and the liquid saturated with sulphurous acid gas, and heated to the boiling point. The selenic acid is thereby reduced, and the selenium precipitated in red flakes, while the sulphate of potash remains in solution. (Wöhler.*)

Modifications of Selenium. — Berzelius found that selenium solidifies in the amorphous state by sudden, and in the crystalline state by slow cooling. Hittorff finds that crystalline (or granular) selenium melts at 211·5°C. (412·6°F.), without previous softening. The mass, when left to cool slowly, remains fluid below that temperature, and solidifies very gradually in the amorphous state; a thermometer immersed in it

* Traité de Chimie générale, par Pelouze et Fremy, 2me. edition, i. 430.

during the cooling does not remain stationary at any point, or indicate any temperature at which the latent heat of the selenium is set free. Amorphous selenium retains its condition for a long time at ordinary temperatures; but between 80° and 217°C. (176° and 412·6°F.), it becomes crystalline and gives out great heat, most quickly between 125° and 180°C. (257° and 356°F.), and when pulverised. When amorphous selenium is heated in an air-bath to between 125° and 130° C., a thermometer immersed in it rises suddenly to between 210° and 215°C. Selenium, as precipitated in the red, finely divided state from selenious acid by sulphurous acid and other reducing agents, or from an aqueous solution of seleniuretted hydrogen by exposure to the air, is amorphous, and exhibits the above-mentioned spontaneous rise of temperature when heated. Selenium deposited from solutions of selenide of potassium or ammonium by exposure to the air, is crystalline, and has a sp. gr. of 4·808 at 60°F. These modifications of selenium are analogous to those of sulphur (p. 679). Berthelot finds that selenium deposited at the positive pole in the electrolysis of hydroselenic acid, is soluble in bisulphide of carbon; but that which is deposited at the negative pole in the electrolysis of selenious acid is insoluble. Amorphous selenium does not conduct electricity; crystalline selenium conducts it much better, and its conducting power increases rapidly with its temperature. (Hittorff.*)

Quantitative estimation of Selenium.—The methods for the estimation and separation of selenium are similar to those which are applied to tellurium (p. 201). When in the form of selenious acid, it is precipitated in the free state by sulphurous acid. Selenic acid must first be reduced to selenious acid by heating with hydrochloric acid; it may also be precipitated as a baryta-salt, like sulphuric acid. Selenious and selenic acid may be separated from certain metals, iron,

* Pogg. Ann. lxxxiv. 214.

zinc, &c., by hydrosulphuric acid, which throws down sulphide of selenium; from others, such as copper, silver, and lead, by sulphide of ammonium, which dissolves sulphide of selenium. Metallic selenides may be decomposed by heating them in a current of chlorine gas, the volatile chloride of selenium being received in water, which decomposes it and precipitates the selenium.

PHOSPHORUS.

Red or amorphous Phosphorus (I. 431). — When phosphorus is subjected to the action of the sun's rays, or to a high temperature in vacuo, or in a gas which does not act upon it chemically, it quickly assumes a red colour, and becomes completely altered in its properties. This modified phosphorus may be obtained in considerable quantity by heating ordinary phosphorus to 230°—250° C. (446°—482° F.) in a retort filled with nitrogen or carbonic acid, and having adapted to its beak a bent tube which dips under mercury. Part of the phosphorus condenses on the neck of the retort in the ordinary state, but the rest is transformed in the course of a few hours into a dark-red mass, which is a mixture of amorphous and ordinary phosphorus. On treating this mixture with bisulphide of carbon, the latter is dissolved, and the amorphous phosphorus remains in form of a red powder.

This amorphous phosphorus differs remarkably from ordinary phosphorus, both in its physical and in its chemical properties. Its sp. gr. at 10° C. (50° F.) is 1·964, while that of ordinary phosphorus is between 1·826 and 1·840; it sinks in melted phosphorus, the density of that liquid at 45° C. being 1·88. It melts at 250° C., and at 260° is reconverted into ordinary phosphorus. Red phosphorus is much less energetic in its chemical affinities than ordinary phosphorus. At ordinary temperatures it has no perceptible odour, and may be exposed to the air without alteration. It does not become luminous in the air till heated to 200° C., or take fire below

260°. It does not combine with melted sulphur. It combines with chlorine without emission of light; with bromine, however, it exhibits that phenomenon. It is insoluble in bisulphide of carbon, alcohol, ether, rock-oil, and terchloride of phosphorus. Oil of turpentine and a few other liquids dissolve small quantities of it (Schrötter*).

Amorphous phosphorus may be obtained in the compact state by keeping phosphorus for several days at a temperature a little below 260° C. It is then converted into a brittle, easily friable, reddish-brown mass, having a conchoïdal fracture, and exhibiting on the fractured surface, an iron-grey colour and imperfect metallic lustre. As thus prepared, however, it is not quite pure, but contains a small quantity of ordinary phosphorus, which causes it to oxidate at ordinary temperatures. The density of this compact red phosphorus was found to be between 2·089 and 2·106; if quite pure, it would be still denser (Schrötter†).

Phosphorus may also be brought to the amorphous state by heating it with a small quantity of iodine. When phosphorus is melted in a glass vessel filled with carbonic acid gas, and a small quantity of iodine introduced through an upright glass tube reaching nearly to the phosphorus, a violent action takes place, attended with great rise of temperature, and a hard, black, semi-metallic mass is produced, which yields a red powder. The same result is obtained when phosphorus is melted under strong hydrochloric acid, and a small quantity of iodine added; under water the experiment does not succeed. The product thus obtained is nearly pure amorphous phosphorus, containing only a trace of iodine; when strongly heated, it distils over almost without alteration, the distillate containing only a trace of ordinary phosphorus. The mode of its formation appears to be this: — An iodide of phosphorus is first formed, probably PI_2, and the phosphorus contained in it passes into

* Wien. Akad. Ber. 1848, 130; Ann. Ch. Phys. [3], xxiv. 406.

† Pogg. Ann. lxxxi. 299; Compt. rend. xxxi. 138.

the amorphous state; this compound is then decomposed, the amorphous phosphorus separated, and a more volatile iodine compound formed, which acts upon another portion of phosphorus with the same final result, so that by repetition of these processes a large quantity of phosphorus may be brought into the amorphous state (Brodie*). Amorphous phosphorus thus prepared differs in some respect from that which is obtained by the action of heat, being more readily attacked by potash, and precipitating certain metallic solutions (*e.g.* sulphate of copper), an effect which may perhaps be due to the small quantity of iodine contained in it. The sp. gr. of this amorphous phosphorus is 2·23.

The formation of amorphous phosphorus under the influence of iodine shows that it possesses an electro-positive character, like amorphous sulphur; a conclusion which is further confirmed by its formation in a similar manner under the influence of bromine and chlorine, and by the imperfect combustion of phosphorus or phosphuretted hydrogen (Berthelot). According to Schrötter, the substance usually regarded as oxide of phosphorus, P_2O, is nothing more than amorphous phosphorus.

Atomic weight of Phosphorus. — By burning amorphous phosphorus in oxygen-gas, Schrötter finds that the atomic weight of phosphorus is 31.†

Modifications of Metaphosphoric acid (I. 449).—This acid appears to be susceptible of five polymeric modifications, viz.:

Monometaphosphoric acid	$HO.PO_5$
Dimetaphosphoric acid	$2HO.2PO_5$
Trimetaphosphoric acid	$3HO.3PO_5$
Tetrametaphosphoric acid	$4HO.4PO_5$
Hexametaphosphoric acid	$6HO.6PO_5$

The formulæ of these several modifications are deduced

* Chem. Soc. Qu. J. v. 289.

† Ann. Ch. Phys. [3], xxxviii. 131.

chiefly from the relative numbers of atoms of the two bases in the double salts which they form.

Monometaphosphoric acid is the variety discovered by Maddrell. It is produced in combination with potash, when that alkali and phosphoric acid are ignited together in equivalent proportions,—and, in combination with oxide of ammonium, by heating dimetaphosphate of ammonia to 250° C. (482° F.) It does not form any double salts, and probably therefore contains only one atom of acid and base: $MO.PO_5$.

Dimetaphosphoric acid is produced when phosphoric acid is heated with oxide of copper, zinc, or manganese in equal or nearly equal numbers of atoms. The copper-salt, which serves for the preparation of all the others, is obtained by heating to 350° C. (662° F.) a solution of phosphoric acid and oxide of copper in the proportion of $5PO_5$ to $4CuO$. It is a crystalline powder, insoluble in water, but soluble, with the aid of heat, in sulphuric acid and in ammonia. The dimetaphosphates of the alkalies, which are obtained by treating the copper-salt with sulphide of potassium, &c., are soluble in water, crystallisable, and converted by heat into insoluble salts. Dimetaphosphoric acid has a strong tendency to form double salts, all of which contain equal numbers of atoms of the two bases; $(MO.M'O).2PO_5$; hence its composition is inferred. For example, on mixing a concentrated solution of the potash-salt with chloride of sodium, or of the soda-salt with chloride of potassium, a crystalline double salt is obtained, having the composition $(NaO.KO).2PO_5 + 2HO$; and by mixing 2 at. dimetaphosphate of ammonia with 1 at. chloride of copper, in tolerably concentrated solutions, and adding alcohol, blue needle-shaped crystals are formed, containing $(CuO.NH_4O).2PO_5 + 4HO$.

Trimetaphosphoric acid is produced in the form of a soda-salt by slowly cooling a fused mixture of 1 at. PO_5 and 1 at. soda. Its double salts contain 2 atoms of one base to 1 atom of the other: $(2MO.M'O).3PO_5$.

Tetrametaphosphoric acid is formed by heating phosphoric acid with oxide of lead, bismuth, or cadmium, or with a mixture of equal numbers of atoms of soda and oxide of copper. The lead-salt is easily decomposed by alkaline sulphides, and yields the corresponding salts of the alkalies. The soda-salt in combination with water is viscid and elastic, and forms with a larger quantity of water a gummy mass, which will not pass through a filter. The double salts of this acid contain equal numbers of atoms of their two bases, like those of dimetaphosphoric acid; but as they differ in physical properties from those of the latter, it is probable that they are composed according to the formula $(2MO.2M'O).4PO_5$, *e. g.* the copper and sodium salt $= (2CuO.2NaO).4PO_5$.

Hexametaphosphoric acid is the first discovered modification of metaphosphoric acid (see page 442). It is formed by igniting the hydrate of phosphoric acid, by the sudden cooling of the soda-salt, and by igniting phosphoric acid with oxide of silver. It forms double salts, the quantities of base in which are nearly in the proportion of 5 at. : 1 at.; hence the composition of these salts is inferred to be: $(5MO.M'O).6PO_5$; thus the soda and lime-salt is $(5CaO.NaO).6PO_5$ (Fleitmann*).

Action of Water at high temperatures on the Pyrophosphates and Metaphosphates.—These salts heated with water in sealed tubes to 280° C. (536° F.), are decomposed, with formation of tribasic phosphates. If the base of the pyrophosphate forms an insoluble tribasic phosphate, the latter is precipitated, and an acid phosphate remains in solution. Thus, with pyrophosphate of silver: $2(2AgO.PO_5) + 2HO = 3AgO PO_5 + (AgO.2HO).PO_5$.

If the base of the pyrophosphate forms a soluble tribasic phosphate, the product is a neutral tribasic phosphate: thus

$$2KO.PO_5 + HO = (2KO.HO).PO_5.$$

* Pogg. Ann. lxxviii. 233, 238.

The metaphosphates similarly treated yield insoluble phosphates and free phosphoric acid, which dissolves small quantities of the precipitated phosphates; thus with lime:

$$3(CaO.PO_5) + 6HO = 3CaO.PO_5 + 2(3HO.PO_5).$$

The metaphosphates of potash and soda yield acid phosphates:

$$NaO.PO_5 + 2HO = NaO.2HO.PO_5.*$$

Sulphides of Phosphorus.—These compounds are easily obtained by fusing sulphur with amorphous phosphorus in an atmosphere of carbonic acid; a violent action takes place, but no explosion (Kekulé †).

Amides of Phosphoric acid.—1. *Triphosphamide,* $N_3H_6PO_2 = N_3\left\{\begin{matrix} PO_2 \\ H_3 \\ H_3 \end{matrix}\right.$.— When dry ammoniacal gas is slowly passed into oxychloride of phosphorus (chloride of phosphoryl, $PO_2.Cl_3$), and the product afterwards treated with water, a solution of sal-ammoniac is obtained, together with a snow-white, amorphous insoluble substance, which is triphosphamide:

$$PO_2Cl_3 + 6NH_3 = 3NH_4Cl + N_3H_6PO_2.$$

This compound is scarcely attacked by continued boiling with water, potash-ley, or dilute acids. It is very slowly decomposed by boiling with strong nitric or hydrochloric acid, more readily by aqua-regia. Strong sulphuric or nitrosulphuric acid dissolves it easily at a gentle heat, forming a solution which contains ammonia and phosphoric acid. It is not completely decomposed by heating with soda-lime. When fused with hydrate of potash, it gives off a large quantity of ammonia, and leaves phosphate of potash. Heated alone, out of contact of air, it also gives off ammonia, and leaves mono-

* A. Reynoso, Compt. rend. xxxiv. 795.

† Proc. Roy. Soc. vii. 38.

phosphamide, which, on being heated with potash, evolves more ammonia, and leaves phosphate of potash. The compound may be regarded as tribasic phosphate of ammonia *minus* 6 at. water: —

$$\left.\begin{matrix}PO_2\\(NH_4)_3\end{matrix}\right\} O_6 \; - \; 6HO \; = \; N_3\left\{\begin{matrix}PO_2\\H_6\end{matrix}\right.$$

By the action of anhydrous aniline, $N.\overbrace{(C_{12}H_5).H.H}$, on oxychloride of phosphorus, the homologous compound *triphenylphosphamide*, $N_3.\overbrace{PO_2.(C_{12}H_5)_3.H_3}$, is obtained; it is a white mass, more easily decomposable than triphosphamide. *Trinaphtylphosphamide*, $N.\overbrace{PO_2.(C_{20}H_7)_3.H_3}$, is obtained in like manner by the action of naphtylamine, $N.\overbrace{(C_{20}H_7).H.H}$, on oxychloride of phosphorus.

Sulphotriphosphamide, $N_3.\overbrace{PS_2.H_3}.H_3$, is obtained by treating sulphochloride of phosphorus, PS_2Cl_3, with ammoniacal gas; it is also a white mass, which is decomposed by water, with evolution of hydrosulphuric acid gas. *Sulphotriphenylphosphamide*, $N_3.\overbrace{PS_2.(C_{12}H_5)_3}H_3$, is obtained in like manner, by the action of aniline on sulphochloride of phosphorus. (Hugo Schiff.*)

2. *Biphosphamide*, $N_2H_3PO_2 = N_2.\overbrace{PO_2.H_3}$. (Gerhardt's Phosphamide.†) — Obtained by saturating pentachloride of phosphorus with ammoniacal gas, and then boiling with water. Chlorophosphamide, $N_2H_4PCl_3$, appears to be first formed, and afterwards resolved by water into hydrochloric acid and biphosphamide:

$$PCl_5 \; + \; 2NH_3 \; = \; N_2H_4PCl_3 \; + \; 2HCl.$$

and: $$N_2H_4PCl_3 \; + \; 2HO \; = \; N_2H_3PO_2 \; + \; 3HCl.$$

The product is purified by boiling, first with caustic potash,

* Ann. Ch. Pharm. ci. 300.

† Ann. Ch. Phys. [3], xviii. 188.

then with nitric or sulphuric acid, and finally, by washing with water. It is a white powder, insoluble in water, alcohol, and oil of turpentine. When heated without access of air, it gives off ammonia, and leaves monophosphamide; but if moisture be present, it yields ammonia and metaphosphoric acid. Fused with hydrate of potash, it gives off ammonia and leaves phosphate of potash. It resists the action of most oxidising agents; but is slowly oxidised by fusion with nitre, and deflagrates with chlorate of potash. It may be regarded as bi-ammoniacal phosphate of ammonia (the so-called neutral phosphate,) *minus* 6HO:—

$$\left.\begin{matrix} PO_2 \\ (NH_4)_2 . H \end{matrix}\right\} O_6 - 6HO = N_2\left\{\begin{matrix} PO_2 \\ H_3 \end{matrix}\right. .$$

Liebig and Wöhler, who discovered this compound, supposed it to be a bihydrate of phosphide of nitrogen, $PN_2 . 2HO$.

3. *Monophosphamide*, $N . PO_2$. (Gerhardt's Biphosphamide.) — Obtained by heating triphosphamide or biphosphamide, without access of air:—

$$N_3H_6PO_2 - 2NH_3 = N.PO_2$$

and: $$N_2H_3PO_2 - NH_3 = N.PO_2$$

It is a pulverulent substance, resembling triphosphamide in its reactions, but still more difficult to decompose (Gerhardt, Schiff). It may be regarded as ammonia, NH_3, in which the 3 at. hydrogen are replaced by the tribasic radical, PO_2, or as mono-ammoniacal phosphate of ammonia (the so-called acid phosphate), *minus* 6HO:—

$$\left.\begin{matrix} PO_2 \\ (NH_4) . H_2 \end{matrix}\right\} O_6 - 6HO = NPO_2.$$

4. *Phosphamic acid*, $NH_2PO_4 = \left.\begin{matrix} N . \overbrace{H . PO_2} \\ H \end{matrix}\right\} O_2$. — This compound, which may be regarded as hydrated oxide of ammonium, $\left.\begin{matrix} NH_4 \\ H \end{matrix}\right\} O_2$ in which 3 at. hydrogen in the ammonium

are replaced by PO_2, is obtained by the action of ammoniacal gas on anhydrous phosphoric acid:—

$$\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O_6 + 2NH_3 = 2\left.\begin{matrix}N.\widetilde{H.PO_2}\\H\end{matrix}\right\}O_2 + 2HO.$$

Great heat is evolved, and the product, when cold, is a fused mass, consisting of phosphamic acid and phosphamate of ammonia, generally mixed with red phosphorus. On dissolving this mass in water, and filtering, a solution is obtained, from which the other salts, most of which are insoluble, may be formed by double decomposition. The free acid, which may be obtained by decomposing the lime-salt with sulphuric acid, is a semi-solid, amorphous mass, which dissolves easily in water and alcohol, and when heated, gives off ammonia, and leaves phosphoric acid.

The phosphamates of the earths and heavy metals, are insoluble in water, and very sparingly soluble in acids, a character which distinguishes them from the phosphates. The ammonia-salt gives white precipitates with salts of barium, strontium, calcium, magnesium, iron, manganese, zinc, lead, mercury, and silver, rose-coloured with cobalt, greenish-white with nickel, light-blue with copper, and dirty green with chromium salts. The iron salt, $NHFePO_4$, dissolves in ammonia, forming a deep purple solution, which on evaporation leaves a crystalline salt, the *phosphamate of ferrammonium*, $\left.\begin{matrix}NH.PO_2\\NH_3Fe\end{matrix}\right\}O_2$. The phosphamates of cobalt, nickel, zinc, copper, mercury and silver likewise dissolve in ammonia, apparently with formation of analogous salts. (Schiff.*)

5. *Phospham*, $N_2P.H$ — When anhydrous phosphoric acid, saturated as completely as possible with ammoniacal gas, is heated in a dry current of that gas, it is decomposed, and on treating the mass when cold with water, phosphoric acid

* Ann. Ch. Pharm. ciii. 168.

dissolves, and there remains a small quantity of a yellowish red residue, which gives off ammonia when fused with potash, and exhibits in other respects, the characters of phospham (Liebig and Wöhler's phosphide of nitrogen, I. 454). This compound is the nitrile of phosphamic acid, being related to it in the same manner as aceto-nitrile, $N . C_4H_3$, to acetic acid (Schiff):—

$$NH(NH_4)PO_4 - 4HO = N_2PH.$$

Gladstone*, by the action of alkalies on chlorophosphide of nitrogen (p. 710), obtained two acids, *azophosphoric* and *deutazophosphoric* acids, which he regarded as phosphoric acid conjugated with one and two atoms of the group PN. Thus phosphoric acid, $= PO_5$; azophosphoric acid, $= PN.PO_5$; deutazophosphoric acid, $= (PN)_2.PO_5$. These acids, according to Gladstone's analyses, are both tribasic, the formula of the azophosphates being $3MO . P_2NO_5 = P_2NM_3O_8$: and that of the deutazophosphates, $3MO . P_3N_2O_5 = P_3N_2M_3O_8$. It is probable, however, that deutazophosphoric acid is the same as Schiff's phosphamic acid.

The formation of deutazophosphoric acid from chlorophosphide of nitrogen ($N_2P_3Cl_5$), is represented, according to Gladstone, by the equation—

$$N_2P_3Cl_5 + 5HO = 5HCl + P_3N_2O_5.$$

Laurent, however, has shown that the formula of chlorophosphide of nitrogen is more probably $NPCl_2$; and from this it is easy to deduce the formation of phosphamic acid:—

$$NPCl_2 + 4HO = 2HCl + NH_2PO_4.$$

Moreover the analysis of the deutazophosphates of baryta and silver agree with the formulæ of the phosphamates $NHMPO_4$ quite as well as with Gladstone's formula. By

* Chem. Soc. Qu. J. iii. 135, 353.

decomposing chlorophosphide of nitrogen with ammonia, Gladstone obtained in three experiments, 181, 183, and 177 per cent. of an ammoniacal salt. Regarding this as phosphamate of ammonia, and representing its formation by the equation—

$$NPCl_2 + 3\left.\begin{matrix}NH_4\\H\end{matrix}\right\}O_2 = \left.\begin{matrix}NHPO_2\\NH_4\end{matrix}\right\}O_2 + 2NH_4Cl + 2HO,$$

the quantity should be 175 per cent., which agrees nearly with the experimental result.

Azophosphoric acid, which appears to be a product of the decomposition of deutazophosphoric acid, is most probably *pyrophosphamic acid*, $\left.\begin{matrix}N_3H_8 . \overbrace{P_2O_6}\\H_3\end{matrix}\right\}O_6$, the tribasic amidogen acid of quadribasic pyrophosphoric acid, $P_2H_4O_{14}$.

Quantitative estimation of Phosphorus and its compounds.—Phosphorus is always estimated in the form of phosphoric acid. When it occurs in combination with a metal, or in an organic compound, or as phosphorous or hypophosphorous acid, it is brought to the highest state of oxidation by treatment with nitric acid, aqua-regia, or a mixture of hydrochloric acid and chlorate of potash.

The precipitation of phosphoric acid (tribasic) from an aqueous solution, in which it exists in the free state or combined with an alkali, is best effected by the addition of sulphate of magnesia and excess of ammonia, chloride of ammonium being likewise added to prevent the precipitation of magnesia in the form of hydrate. The phosphoric acid is then precipitated as phosphate of magnesia and ammonia, $NH_4O.2MgO.PO_5$. The precipitate does not settle down at once, but its deposition may be accelerated by leaving the vessel in a warm place. Care must be taken, however, not to allow the liquid to become very hot, as in that case hydrate of magnesia will be precipitated, and will be very difficult to redissolve. The precipitate, after standing for about

two hours, is collected on a filter and washed with water containing ammonia, as pure water decomposes it. It is then dried and ignited, whereby it is converted into pyrophosphate of magnesia, $2MgO.PO_5$, containing 63·67 per cent. of phosphoric acid, PO_5, and 27·98 per cent. of phosphorus.

If the phosphoric acid is in the monobasic or bibasic modification, it must first be converted into the tribasic acid by fusing the salt with five or six times its weight of carbonate of soda, or, better, with a mixture of carbonate of potash and carbonate of soda in equivalent proportions. The mixture may then be fused over a lamp, whereas if carbonate of soda or carbonate of potash alone be used, the heat of a furnace will be required. By this fusion with excess of an alkaline carbonate, the phosphoric acid is in most cases completely separated from any other base with which it may be combined, and converted into a tribasic phosphate of the alkali, which may then be treated as above.

Phosphates which are insoluble in water, may be dissolved in nitric or hydrochloric acid; and from these solutions, the bases may in some cases be precipitated by hydrosulphuric acid, in others by sulphide of ammonium, and the phosphoric acid subsequently precipitated from the filtered solution in the form of the ammonio-magnesian phosphate in the manner above described.

To separate phosphoric acid from the *earths*, other methods are required. From *baryta* it is easily separated by sulphuric acid, which throws down the baryta; from *strontia* and *lime*, also, by sulphuric acid with addition of alcohol. From *magnesia* it may be separated by fusion with a mixture of carbonate of potash and carbonate of soda in equivalent proportions. From *alumina* it is most readily separated by dissolving the compound in hydrochloric acid, adding sufficient tartaric acid to keep the alumina in solution when the liquid is neutralised by an alkali, and then adding excess of ammonia and sulphate of magnesia, whereby a precipitate of ammonio-magnesian

phosphate is produced, which may be treated as already described. This method may also be applied to the separation of phosphoric acid from iron.

When phosphoric acid exists in combination with several earthy bases together, it may be separated by dissolving the compound in nitric acid, adding metallic mercury in slight excess, evaporating over the water-bath to perfect dryness, and treating the residue with water. The whole of the phosphoric acid then remains undissolved in the form of mercurous phosphate, while the bases pass into the solution as nitrates. (H. Rose.) This method, however, requires attention to a number of details and precautions which cannot here be given.

Another method of separating phosphoric acid from a mixture of bases, by means of acetate of uranium, has already been described (II. 258).

The salts of phosphorous and hypophosphorous acid may be oxidised by nitric acid, the former being thereby converted into pyrophosphates, the latter into metaphosphates. These salts must then be converted into tribasic phosphates in the manner above described.

Phosphorous and hypophosphorous acid may also be estimated by their power of precipitating gold in the metallic state from its solutions, or, better, by their reducing action on mercuric chloride, which, when present in excess, is reduced to mercurous chloride.

CHLORINE.

Chloride of Nitrogen (I. 481).—According to Bineau *, this compound is NCl_3, that is to say, ammonia in which all the hydrogen is replaced by chlorine. Bineau's analysis gives 10·6 p.c. N, and 89·3 Cl; the formula requires 11·65 N, and

* Ann. Ch. Phys. [3], xv. 71.

88·35 Cl. According to Porrett, Wilson, and Kirk *, it is $NHCl_3$; according to Gladstone †, N_2HCl_5, or $NHCl_2 + NCl_3$.

Sulphite of Perchloride of Carbon, $C_2Cl_4.2SO_2$.—This body was discovered by Berzelius and Marcet, who obtained it by the action of aqua-regia on bisulphide of carbon; but a better mode of obtaining it is the following:—A bottle, capable of holding about three pints, is half filled with a mixture of peroxide of manganese and hydrochloric acid; about 800 grains of bisulphide of carbon are then added; the vessel quickly closed, and left for some days in a cool place. It is then exposed for several days longer to a temperature of 30° C. (86° F.), or in summer to direct sunshine, and frequently shaken, till the greater part of the bisulphide of carbon is converted into the new compound. The action may be greatly accelerated by adding a quantity of nitric acid equal in weight to twice that of the bisulphide of carbon used. The mixture is then distilled, whereupon undecomposed bisulphide of carbon first passes over, together with chloride of sulphur and a peculiar yellow liquid ($C_4S_4Cl_4$), and afterwards the sulphite of perchloride of carbon condenses in the solid form in the neck of the retort. The formation of this compound is represented by the following equation:—

$$2CS_2 + 8Cl + 4HO = C_2Cl_4.2SO_2 + 4HCl + 2S.$$

Sulphite of perchloride of carbon is a white crystalline solid having a highly pungent odour, and exciting tears. It melts at 135° C. and boils at 170°; may be sublimed, and forms small rhombohedral crystals. It is soluble in alcohol, ether, and bisulphide of carbon; insoluble in water. It is decomposed at a dull red heat, yielding chlorine, sulphurous acid, and protochloride of carbon:—

* Gmelin's Handbook, ii. 472.

† Chem. Soc. Qu. J. vii. 51.

$$2(C_2Cl_4 \,.\, 2SO_2) = 4Cl + 4SO_2 + 2C_2Cl_2.$$

It decomposes slowly in contact with water or moist air, yielding sulphurous, sulphuric, carbonic, and hydrochloric acids. Heated with a large excess of strong sulphuric acid, it gives off sulphurous acid, anhydrous sulphuric acid, hydrochloric acid, and phosgene gas:—

$$C_2Cl_4 \,.\, 2SO_2 + 2SO_4H = 2SO_2 + 2SO_3 + 2HCl + 2COCl.^*$$

Chlorosulphide of Carbon $C_4S_4Cl_4$.—The liquid distillate obtained in the preparation of the preceding compound contains this substance, which may be obtained from it in a state of purity by repeated distillation with water and hydrate of magnesia, which decomposes the chloride of sulphur. It may also be prepared by exposing bisulphide of carbon to sunshine in an atmosphere of dry chlorine—

$$CS_2 + 2Cl = SCl + CSCl,$$

and purified as above. Also by passing a mixture of hydrosulphuric acid gas and vapour of perchloride of carbon through a red-hot tube:—

$$2C_2Cl_4 + 4HS = 4HCl + C_4S_4Cl_4.$$

It is a yellow liquid, not miscible with water; has a peculiar and powerful odour, and irritates the eyes very strongly; Sp. gr. 1·46. It boils at 70° C. (158° F.). It is not decomposed by water or acids, not even by nitric acid. Bisulphide of carbon and caustic potash decompose it gradually. It absorbs ammoniacal gas (Kolbe†).

Sulphite of Protochloride of Carbon, $C_2Cl_2 \,.\, 2SO_2$.—Formed by the action of reducing agents, viz., sulphurous acid, hydro-sulphuric acid, zinc, iron, proto-chloride of tin, &c., on the sulphite of perchloride of carbon. It has not been obtained in the anhydrous state. It dissolves in water and alcohol, and is best prepared in the state of solu-

* Kolbe, Ann. Ch. Pharm. liv. 148.

† Ibid. xlv. 53.

tion, by passing sulphurous acid gas through an alcoholic solution of sulphite of perchloride of carbon. The solution is colourless and inodorous, has an acid reaction, and absorbs oxygen rapidly, forming sulphuric acid and phosgene: —

$$C_2Cl_2.2SO_2 + 4O = 2SO_3 + 2COCl.$$

Chlorine converts it into $C_2Cl_4 . 2SO_2$. (Kolbe.)

Perchlorocarbosulphurous acid, $C_2Cl_3O . 2SO_2 . HO$.—Formed by the action of caustic alkalies on sulphite of perchloride of carbon:—

$$C_2Cl_4.2SO_2 + 2KO = C_2Cl_3O.2SO_2.KO + KCl.$$

The hydrated acid is obtained by decomposing the baryta-salt with sulphuric acid. It crystallises in small deliquescent prisms, which may be partially sublimed without decomposition. They contain 2 at. water of crystallisation, their formula being $C_2Cl_3O.2SO_2.HO + 2HO$. The acid is not decomposed by fuming nitric acid or aqua-regia, and is so powerful an acid that it expels hydrochloric acid from its combinations. Its salts are all soluble in water and alcohol, and crystallise with facility. When heated they are resolved into phosgene, sulphurous acid, and a metallic chloride; *e. g.*

$$C_2Cl_3O.2SO_3.KO = 2COCl + 2SO_2 + KCl.$$

Chlorocarbosulphurous acid, $C_2Cl_2.2SO_2.2HO$. — Formed by the action of alkalies on sulphite of protochloride of carbon, or by the action of zinc on the preceding acid. Resembles the preceding in most of its properties. Its salts, when heated, give off phosgene, sulphurous acid, and water, and leave a residue of metallic chloride and charcoal.

Chloromethylosulphurous acid, $C_2HCl . 2SO_2 . 2HO$.—Formed by the continued action of nascent hydrogen on chlorocarbosulphurous acid: —

$$C_2Cl_2.2SO_2.2HO + H = C_2HCl . 2SO_2.2HO + HCl.$$

When zinc is immersed in an aqueous solution of chlorocarbosulphurous acid, it dissolves with evolution of hydrogen; and the hydrogen, as it is set free, converts part of the acid into chloromethylosulphurous acid; but complete transformation can only be obtained by subjecting an acidulated solution of a perchlorocarbosulphite or chlorocarbosulphite to the action of the galvanic current. The hydrated acid is a viscid, strongly acid liquid, which bears a heat of 140° C. without decomposition; at $-16{\cdot}6°$ C. it becomes syrupy; in other respects it resembles perchlorocarbosulphurous acid. All its salts are soluble in water, and crystallisable.

Methylosulphurous acid, $C_2H_3O.2SO_2.HO$.—Formed when a neutral solution of perchlorocarbosulphite of potash is decomposed by the electric current, the electrodes being formed of amalgamated zinc plates:—

$$C_2Cl_3O.2SO_2.KO + 6Zn + 6HO = C_2H_3O.2SO_2.KO + 6ZnO + 3HCl.$$

Also when an amalgam of potassium is immersed in the same solution,

$$C_2Cl_3O.2SO_2.KO + 6K + 3HO = C_2H_3O.2SO_2.KO + 3KCl + 3KO.$$

The concentrated solution of the hydrated acid is a sour, inodorous, viscid liquid, which may be heated to nearly 130° C. without decomposition, but at that temperature begins to turn brown and decompose. It does not crystallise when pure. It is equal to perchlorocarbosulphurous acid in stability and in affinity for bases. Its salts are soluble and crystallisable. (Kolbe.*)

Intermediate Chloride of Sulphur, S_4Cl_3.—Protochloride of sulphur is readily decomposed by heat, its boiling point rising quickly from 64° to 78° C., where it remains stationary.

* Ann. Ch. Pharm. liv. 143.

The deep orange-yellow liquid thus obtained appears to be composed of $S_4Cl_3 = S_2Cl + 2SCl$.

Terchloride of Sulphur, SCl_3. — Not known in the separate state, but exists in the compound $SCl_3 . 5SO_3$, obtained by mixing the protochloride of sulphur, SCl, with Nordhausen sulphuric acid, and distilling. Sulphurous acid and anhydrous sulphuric acid pass over first, then the compound $SCl_3 . 5SO_3$, while monohydrated sulphuric acid remains in the retort. The compound $SCl_3 . 5SO_3$ is a colourless oily liquid having a peculiar odour, and fuming slightly in the air. Its density is 1·818, and that of its vapour 4·481. Boils at 145° C. (283° F.). Water decomposes it rapidly, forming sulphuric and hydrochloric acids. (H. Rose.)

Chlorosulphuric acid, SO_2Cl, is regarded by some chemists as a bisulphate of terchloride of sulphur, $SCl_3 . 2SO_3$.*

Sulphate of Bichloride of Sulphur, $SCl_2 . SO_3 = S_2Cl_2O_3$. —Formed by the action of moist chlorine gas on protochloride of sulphur. Large transparent colourless crystals, which are decomposed by alcohol and water, or even by exposure to damp air. Enclosed in a sealed glass tube, they change in the course of a few months into a very mobile, slightly yellow liquid, which has the same composition as the crystals, but does not solidify at −18° C. (0° F.). It is dissolved by water, with formation of sulphuric and hydrochloric acids. The compound $S_2Cl_2O_3$ may be regarded as hyposulphuric acid in which 2 at. O are replaced by chlorine. (Millon.†)

Chlorosulphide of Phosphorus, $PS_{10}Cl_4$.—Besides the chlorosulphide of phosphorus described on page 487, Vol. I., another compound of these elements, having the formula just given, is obtained by passing a stream of phosphuretted hydrogen into dichloride of sulphur. This compound is a yellow syrupy liquid, which is decomposed by water, with

* See Vol. I., page 411, line 4, where, however, there is a misprint, the formula being given as $3SO_3 . SCl_3$ instead of $2SO_3 . SCl_3$.

† Ann. Ch. Pharm. lii. 230; lxxvi. 235.

evolution of hydrosulphuric acid and deposition of sulphur. It may be regarded as a compound of dichloride of sulphur with a peculiar sulphide of phosphorus, not yet isolated:—

$$4S_2Cl + PS_2 = PS_{10}Cl_4.$$

This compound was discovered by H. Rose.

Sulphide of Pentachloride of Phosphorus, $PCl_5 . S_4$.—When a mixture of 3 pts. pentachloride of phosphorus and 1 pt. of sulphur is melted, a colourless liquid is obtained, which boils at about 100° C. It dissolves large quantities of pentachloride of phosphorus and sulphur, the latter of which it deposits in crystals; it is very difficult to purify. Water decomposes it immediately, with formation of a great number of products (Gladstone.*) The compound may be regarded as $PS_2Cl_3 + Cl_2S_2$ (Schiff†).

Action of acids on Pentachloride of Phosphorus. — Persoz and Bloch ‡, by passing dry sulphurous acid gas over pentachloride of phosphorus, obtained a volatile, strongly refracting liquid which they regarded as $PCl_5 . 2SO_2$. According to Schiff §, however, this liquid is decomposed by fractional distillation, being resolved into oxychloride of phosphorus which boils at 110° C. (230 F.), and a more volatile liquid, which passes over at 82° C. (147·6 F.). This latter is the *chloride of thionyl*, $S_2O_2 . Cl_2$, the name thionyl denoting the biatomic radical, S_2O_2, of sulphurous acid and its salts, hydrated sulphurous acid being $\left.\begin{matrix}S_2O_2\\H_2\end{matrix}\right\}O_4$, and anhydrous sulphurous acid $S_2O_2 . O_2$. Chloride of thionyl is a volatile liquid of great refracting power, and having a suffocating odour like that of sulphurous acid. It is decomposed by water, and more readily by alkalies, into hydrochloric and sulphurous acids. With alcohol, it yields hydrochloric and ethylosulphurous acids.

* Chem. Soc. Qu. J. iii. 5.

† Ann. Ch. Pharm. ci. 309.

‡ Compt. rend. xxvii. 86.

§ Ann. Ch Pharm. cii. 111.

Thionamide, $N_2\left\{\begin{matrix}S_2O_2\\H_4\end{matrix}\right.$, is produced when chloride of thionyl is brought in contact with dry ammonia:

$$S_2O_2 . Cl_2 + 4NH_3 = 2NH_4Cl + N_2(S_2O_2)H_4.$$

The action is very violent, but may be moderated by cooling. The product is a white, non-crystalline solid, which gives up sal ammoniac when digested in water, and is afterwards completely decomposed.

Anhydrous sulphuric acid acts upon pentachloride of phosphorus in the same manner as anhydrous sulphurous acid, producing a liquid which Persoz and Bloch regarded as $PCl_5 . 2SO_3$, but which, according to Schiff, is resolved by distillation into oxychloride of phosphorus, and chloride of sulphuryl or chlorosulphuric acid, $S_2O_4 . Cl_2$.

With *hydrated sulphuric acid*, pentachloride of phosphorus forms *chlorohydrated sulphuric acid*, S_2HClO_6:

$$\left.\begin{matrix}S_2O_4\\H_2\end{matrix}\right\}O_4 + PCl_5 = \left.\begin{matrix}S_2O_4\\HCl\end{matrix}\right\}O_2 + HCl + PO_2Cl_3.$$

And this compound, by the further action of the pentachloride, is converted into chlorosulphuric acid, $S_2O_4 . Cl_2$ (p. 551). Chlorohydrated sulphuric acid is a liquid which boils at 145° C., is decomposed by water, yielding hydrochloric and sulphuric acids, and dissolves chloride of sodium at a gentle heat, with evolution of hydrochloric acid and formation of the compound S_2NaClO_6. It effervesces with melted nitre, giving off a vapour (probably NO_4Cl) which smells like aqua-regia, and when passed into water, forms nitric and hydrochloric acids. The compound S_2HClO_6 is probably identical with that which H. Rose obtained by the action of sulphuric acid on pentachloride of sulphur, and regarded as S_2O_5Cl. It is likewise obtained in small quantity by the action of strongly heated platinum-black on an imperfectly dried mixture of chlorine and sulphurous acid. (Williamson.*)

* Proceedings of the Royal Society, vii. 11.

Tungstic acid treated with pentachloride of phosphorus yields oxychloride of phosphorus and an oxychloride of tungsten, $W_2O_4Cl_2$. Similarly with molybdic acid.

Hydrated antimonic acid heated with pentachloride of phosphorus yields hydrochloric acid and oxychloride of phosphorus, with a residue of anhydrous antimonic acid.

Anhydrous phosphoric acid and pentachloride of phosphorus form oxychloride of phosphorus:

$$P_2O_{10} + 3PCl_5 = 5PO_2Cl_3.$$

When strong *nitric acid* is cautiously added to pentachloride of phosphorus, hydrochloric acid is evolved; and if the escaping vapour be passed through a good refrigerating apparatus, a blood-red liquid condenses, which when distilled yields yellowish-red vapours, probably NO_4Cl, and a distillate of oxychloride of phosphorus. (Schiff.)

Chlorophosphide of Nitrogen, $P_2N_2Cl_5$ according to Wöhler and Liebig, who discovered it; $P_3N_2Cl_3$ according to Gladstone; $PNCl_2$ according to Laurent. It is formed by the action of ammonia on pentachloride of phosphorus. On treating the crude product with ether, the chlorophosphide of nitrogen is alone dissolved, and may then be crystallised. It is also produced by distilling a mixture of 1 pt. pentachloride of phosphorus with 2 pts. sal-ammoniac. It may be purified by distillation with water, being carried over by the vapour of water, and then only requires to be dried. It crystallises in rhomboidal prisms; melts at 110°, and boils at 240° C. It is insoluble in water, but dissolves in alcohol, ether, and oil of turpentine. Alkalies decompose it, with formation of phosphamic acid (p. 699).

BROMINE.

Bromide of Nitrogen. — When chloride of nitrogen is gently heated with bromide of potassium, double decomposition takes place, and a brown, very heavy, oily liquid is formed, which appears to be bromide of nitrogen. It is very volatile, has an offensive odour, and irritates the eyes strongly. It detonates easily, and is decomposed by hydrochloric acid, hydrobromic acid, and ammonia. Its composition appears to be NBr_3. (Millon.)

Oxybromide of Phosphorus, PBr_3O_2. — Produced by the decomposition of the pentabromide in moist air. When the thick reddish liquid thus formed is heated, to drive off the hydrobromic acid which it contains, and then distilled at about 180° C. (366° F.), the oxybromide passes over in the form of a colourless heavy liquid, which boils between 170° and 200° C. It does not mix with water, but is slowly decomposed by that liquid, with formation of phosphoric and hydrobromic acids. It dissolves in oil of turpentine, ether, and strong sulphuric acid, and is precipitated from the last-mentioned solution by water. Nitric acid decomposes it, with evolution of bromine. Another body, apparently of the same composition, but solid and crystalline, is sometimes obtained as a residue in the distillation of pentabromide or oxybromide of phosphorus, and by the action of moist air on the pentabromide in an imperfectly-closed vessel. It is decomposed by water, melts and volatilises when heated, but on cooling remains as a liquid, exhibiting the characters of the oxybromide. (Gladstone.*)

Sulphobromide of Phosphorus. — Pentabromide of phosphorus is decomposed by hydrosulphuric acid, with formation of a heavy liquid, which boils without decomposition at 200° C., and appears to have the composition $3PBr_3 . PS_3$; it

* Phil. Mag. [3], xxxv. 345.

may, however, be a mixture of two compounds having nearly the same boiling point. (Gladstone.*)

IODINE.

Natural sources of Iodine.—According to Chatin †, iodine exists in the air, in nearly all water, and in a great number of plants, land and fresh-water as well as marine; also in coal, in various chemical products, viz., commercial potash, soda, and sal-ammoniac, in wine, cider, perry, &c., in milk and eggs. He finds also that iodine is least abundant in the air and water of those localities in which goitre and cretinism prevail. Similar results have been obtained by other chemists. On the other hand, Macadam ‡, Lomeyer §, and others have not been able to detect iodine in the air or in rain-water. Macadam, however, found iodine in commercial potash, in numerous samples of alkaline carbonates (used as reagents), in the ashes of wood-charcoal, in coal, and in numerous plants. Lomeyer examined particularly the air and water of various localities where goitre is scarce, but found no trace of iodine. Chatin ‖ attributes the negative results obtained by Macadam and Lomeyer to defective methods of analysis, but does not give any exact description of his own process.

Hypoiodic acid, IO_4, *and Sub-hypoiodic acid,* $I_5O_{19} = 4IO_3 + IO_7$.—When one part of iodic acid and 5 parts of monohydrated sulphuric acid are heated in a platinum crucible, till oxygen gas and afterwards vapours of iodine are evolved, a green solution is obtained; and on leaving this for some days in a dry atmosphere, a yellow crystalline crust is deposited, which, when freed from the excess of sulphuric acid and washed with water and alcohol, yields sub-hypoiodic acid; and this compound heated to 150° C. gives off vapour of iodine, and

* Phil. Mag. [3], xxxv. 345.
† Compt. rend. xxx. 352; xxxi. 280; xxxii. 669; xxxiii. 519, 529, 581.
‡ Chem. Soc. Qu. J. vi. 166. § Phil. Mag. [4], vi. 237.
‖ J. Pharm. [3], xxv. 192.

is converted into hypoiodic acid. The latter is a sulphur-yellow amorphous powder, which at 180° C. is resolved into iodic acid and iodine. Water and nitric acid decompose it in a similar manner. Sulphuric acid dissolves it with the aid of heat, and on cooling deposits a compound consisting of $IO_4 . 4SHO_4$. Aqueous alkalies decompose hypoiodic acid, forming iodates and the other compounds which result from the action of iodine on alkalies.

Sub-hypoiodic acid bears a considerable resemblance to hypoiodic acid, both in physical and chemical properties. When heated, it gives off iodine and leaves hypoiodic acid. (Millon.)

Iodide of Nitrogen (I. 501).—Gladstone* has analysed this compound (as prepared by precipitating an alcoholic solution of iodine with excess of ammonia and washing with water), and arrived at results which accord with Bineau's formula, NHI_2. By decomposing the compound with hydrosulphuric acid, he finds that it contains 2I to 1N, while its decomposition by aqueous sulphurous acid agrees with the equation,

$$NHI_2 + 4SO_2 + 4HO = NH_3 + 2HI + 4SO_3.$$

Gladstone suggests for the compound the name *iodimide.* He also finds the above formula to be in accordance with the formation of the compound by the action of hypochlorite of lime on iodide of ammonium (observed by Playfair), that reaction being attended with evolution of ammonia, according to the equation,

$$2(CaO.ClO) + 2\,NH_4I = NHI_2 + 2\,CaCl + 4\,HO + NH_3.$$

Bunsen takes a different view of the constitution of iodide of nitrogen. He observes: 1. That the mode of formation of this compound from iodine and ammonia, with hydriodic acid as the only secondary product, shows that it must be a

* Chem. Soc. Qu. J. v. 34.

substitution-product of ammonia, of the form NI_3, NHI_2 or NH_2I, associated at most with ammonia or hydriodic acid; 2. That it cannot contain hydriodic acid, because it dissolves in hydrochloric acid without evolution of gas, and forms a solution containing ammonia and protochloride of iodine, but no hydriodic acid; 3. That, to determine its composition, it is sufficient to ascertain how much ICl and how much NH_3 it yields with hydrochloric acid, and to see which of the following equations agrees with the results:

(*a*) $NI_3 + 3HCl = 3ICl + NH_3$.
(*b*) $NHI_2 + 2HCl = 2ICl + NH_3$.
(*c*) $NH_2I + HCl = ICl + NH_3$.
(*d*) $NH_2I + NH_3 + HCl = ICl + 2NH_3$, &c.

Preparations obtained by mixing cold and more or less saturated anhydrous alcoholic solutions of iodine and ammonia, which were not decomposed by washing with absolute alcohol, gave, when dissolved in hydrochloric acid, quantities of ammonia, iodine, and chlorine, in the atomic proportion of 2 : 3 : 3, showing that the constitution of the compound is $NI_3 + NH_3$. A preparation obtained by adding ammonia to a solution of iodine in aqua-regia diluted with water, and washed as quickly as possible with cold water, gave, with hydrochloric acid, quantities of ammonia and protochloride of iodine in the atomic proportion of 5 : 12, showing that its formula was $4NI_3 + NH_3$. When washed with water for any length of time, even till the greater part of the compound was decomposed, with separation of iodine and nitrogen, the undecomposed portion still yielded more than 1 at. ammonia to 3 at. chloride of iodine, a proof that ammonia enters essentially into its constitution. Bunsen is of opinion that there exist two distinct compounds, $NI_3 . NH_3$ and $4NI_3 . NH_3$, formed in the manner shown by the equations,

$$2NH_3 + 6I = (NI_3 . NH_3) + 3HI;$$
$$4(NI_3 . NH_3) + 3HO = 4NI_3 . NH_3 + 3NH_4O.$$

The formation of the so-called iodide of nitrogen by the action of ammonia on a solution of iodine in aqua-regia, would be inconsistent with this view, if that solution contained, not ICl, but, as is commonly supposed, ICl_3, because NI_3 could not be formed by the action of ammonia upon the latter. Experiment, however, shows that the solution of iodine in aqua-regia contains only ICl. The formation of the so-called iodide of nitrogen from ICl is explained by the equation,

$$2NH_3 + 3ICl = (NI_3 . NH_3) + 3HCl.$$

The immediate products of its explosion are nitrogen and hydriodic acid:

$$NI_3 . NH_3 = 2N + 3HI,$$

which latter is for the most part resolved by the high temperature into iodine and hydrogen, while another portion unites with the ammonia of the compound, forming iodide of ammonium, thereby setting free quantities of iodine and nitrogen equivalent to this ammonia.*

Gladstone, in a subsequent communication†, remarks that his mode of preparing the iodide of nitrogen differs essentially from that of Bunsen, and that his formula NHI_2 may be written $2NI_3 + NH_3$, which shows it to be intermediate between the two formulæ given by Bunsen. He concludes, from further experiments, that the formula NHI_2 is true, not only for the preparation obtained by the method described in his former paper, but likewise for that obtained by precipitation from solutions of iodine and ammonia in absolute alcohol.

Iodides of Phosphorus (I. 502).—These compounds are best prepared by dissolving iodine and phosphorus together in bisulphide of carbon, and cooling the solution till it crystallises. There appear to be only two iodides of phosphorus, viz. PI_2 and PI_3, which are prepared by dissolving the two substances as above, in the respective atomic proportions; if they be mixed

* Chem. Soc. Qu. J. vi. 90.

† Ibid. vii. 51.

in any other proportions, the same compounds crystallise out, together with the excess of iodine or phosphorus.

The *biniodide*, PI_2, is a light-red solid body, which melts at 110° C., forming a red liquid. Water decomposes it, with formation of hydriodic and phosphorous acid, and deposition of yellow flakes. When melted with excess of phosphorus and decomposed by water, it yields red phosphorus. It dissolves in bisulphide of carbon, and is deposited from the solution in flattened prismatic crystals, of a light-orange colour.

The *teriodide*, PI_3, forms dark-red six-sided laminæ, which dissolve very readily in bisulphide of carbon, and rapidly absorb moisture from the air. It melts at 55° C., and crystallises in well-defined prisms on cooling. At a higher temperature, it is decomposed, giving off vapours of iodine. Water decomposes it, with formation of hydriodic and phosphorous acids, and formation of an orange-yellow flaky deposit. (Corenwinder.*)

Estimation and separation of Chlorine, Bromine, and Iodine.— *Chlorine*, in the form of hydrochloric acid or a soluble chloride, is estimated by precipitation with nitrate of silver, the precipitate being treated in the manner described at page 346. The fused chloride contains 24·72 per cent. of chlorine, equivalent to 25·42 of hydrochloric acid.

Many chlorides, chiefly basic or oxychlorides, which are insoluble in water dissolve in nitric acid. The chlorine in such compounds may be precipitated by adding nitrate of silver to the nitric acid solution. Care must, however, be taken not to heat the compound with excess of nitric acid, as in that case a portion of the chlorine may be lost. Some chlorides, as the chloride of silver and dichloride of mercury, are insoluble even in nitric acid. Chloride of silver may be decomposed, either by ignition in a current of hydrogen, by heating it in a porcelain crucible with a mixture of the

* Ann. Ch. Phys. [3], xxx. 242.

carbonates of potash and soda, in equivalent proportions, till the salt just begins to melt, or by treating it with dilute sulphuric acid in contact with a piece of pure zinc (p. 339). Dichloride of mercury is easily decomposed by caustic alkalies.

Chlorates and other oxygen-salts of chlorine may be reduced to chlorides, by ignition, or, better in most cases, by the action of sulphurous or hydrosulphuric acid. The chlorine is then precipitated by nitrate of silver, as above, after the excess of the reducing agent has been removed by means of nitric acid or a ferric salt. [For the methods of determining the quantity of chlorine in bleaching powder and other hypochlorites for commercial purposes, see I. 592, and II. 15; also Bunsen's volumetric method, II. 722.]

The quantity of chlorine in an organic compound is determined by igniting the compound with excess of pure quick lime in a combustion-tube, whereby the chlorine is converted into chloride of calcium. The contents of the tube are then dissolved in dilute nitric acid, and the chlorine precipitated by nitrate of silver.

Bromine is estimated in the form of bromide of silver (containing 42·55 per cent. of bromine), in exactly the same manner as chlorine. Bromates are also reduced to bromides in the same manner as chlorates to chlorides.

When bromine and chlorine occur together, they may both be precipitated by treating the solution with excess of nitrate of silver. The precipitate of chloride and bromide is then ignited and weighed; and a known portion of it is afterwards heated in a current of chlorine gas. The bromide of silver is thereby converted into chloride, the bromine passing off in vapour. The resulting chloride of silver weighs less than the mixture of chloride and bromide by the difference (w) between the weight of the bromine which has escaped and the chlorine which has taken its place; moreover, these weights are to one another as the equivalent weights of bromine and chlorine, that is, as 80 to 35·5. Hence, to deter-

mine the quantities of Br and Cl in the mixed silver-salts, we have the two equations,

$$Br - Cl = w; \quad \frac{Br}{Cl} = \frac{80}{355}$$

whence $$Br = 1{\cdot}8\,w; \quad Cl = 0{\cdot}8\,w.$$

If the quantity of bromine is very small, as in sea-water and salt-springs, in comparison with that of the chlorine, this method does not give very exact results. In such cases it is best to mix the solution, after due concentration, with only enough nitrate of silver to precipitate about one-sixth of the chlorine, and treat the precipitate thus formed,—which is sure to contain the whole of the bromine,—in the manner just described. The remainder of the chlorine is then determined by treating the filtered liquid with excess of nitrate of silver.

According to Mr. F. Field*, chloride of silver is completely decomposed by agitating it with excess of bromide of potassium in solution, the silver being converted into bromide, and the whole of the chlorine passing into the solution. This mode of decomposition might therefore be used instead of the ignition of the mixed precipitate in a current of chlorine. The chloride and bromide of silver are also completely decomposed by iodide of potassium.

Iodine in soluble iodides is estimated by precipitation with nitrate of silver, in the same manner as chlorine and bromine; 100 pts. of iodide of silver contain 54·025 pts. of iodine.

It may also be precipitated as iodide of palladium by mixing the solution with nitrate or chloride of palladium. A black precipitate then falls, which settles down slowly but completely, and when ignited, leaves metallic palladium, 100 pts. of which are equivalent to 23·83 pts. of iodine; or the precipitate may be collected on a weighed filter, dried at 100° C. and weighed; 100 pts. of it contain 7·04 pts. of iodine: but the method by ignition is to be preferred.

* Chem. Soc. Qu. J. x. 234.

This method of precipitation serves also to separate iodine from bromine and chlorine. If the chlorine is also to be estimated, the precipitation must of course be made with nitrate of palladium, not with the chloride. If bromine is present without chlorine, the iodine must be precipitated with chloride of palladium, because the nitrate would precipitate bromine as well as iodine: the precipitation of the bromine may, however, be prevented by the addition of a soluble chloride. To estimate the chlorine and bromine in the filtered liquid, the excess of palladium must be removed by hydrosulphuric acid, and the excess of the latter by means of nitric acid or a ferric salt. The bromine and chlorine may then be precipitated by nitrate of silver, and the precipitate treated in the manner already described.

The methods of treating insoluble iodides are similar to those already given for chlorides (p. 716).

Iodates and periodates are reduced to iodides by the action of sulphurous or hydrosulphuric acid. To decompose them by ignition would not give accurate results, because a portion of the iodine is thereby expelled.

Iodine and bromine in organic compounds are estimated in the same manner as chlorine (p. 717).

FLUORINE.

Sources of Fluorine.—Professor G. Wilson, of Edinburgh, has discovered fluorine in a great number of plants, especially in the siliceous stems of grasses and equisetaceous plants, always however in very small and variable quantities. He supposes that soluble fluorine-compounds diffuse themselves through the rising sap of the plant, and are converted, by the silica therein contained, into insoluble silico-fluorides. Traces of fluorine also occur in the trap-rocks near Edinburgh and in the neighbourhood of the Clyde, in the granites of Aberdeenshire,

and in the soils formed by the disintegration of such rocks.* The same chemist has likewise found fluorine in the ashes of ox-blood, milk, cream-cheese, and very slight traces in the ash of the whey.† For the detection of small quantities of fluorine in rocks, ashes, &c., Professor Wilson heats the substance (mixed with silica if that body be not already present) with strong sulphuric acid in a glass vessel; passes the evolved fluoride of silicon into water; supersaturates the hydrofluosilicic acid thus formed with ammonia; evaporates to dryness; exhausts the residue with water; again evaporates the filtrate; and tests the residue in the ordinary way by treating it with sulphuric acid in a platinum vessel covered with a waxed glass plate.‡

Isolation of Fluorine.—Fremy, by submitting fused fluoride of potassium to the action of the voltaic battery, has eliminated a gas which rapidly attacks platinum, decomposes water with formation of hydrofluoric acid, and displaces iodine from its combinations with metals. By decomposing fluoride of calcium at a red heat with dry chlorine or oxygen, he likewise obtains a gas which rapidly attacks glass. This gas appears to be fluorine.§

Anhydrous hydrofluoric acid may be obtained by heating the fluoride of potassium and hydrogen in a platinum vessel, or by decomposing fluoride of lead on a layer of charcoal in a platinum tube by dry hydrogen gas. It is gaseous at ordinary temperatures; but at the temperature of a mixture of ice and salt, it condenses into a very mobile liquid, which acts violently on water, forms white fumes in the air, and attacks glass. (Fremy.‖)

Estimation of Fluorine.—The solid compounds of fluorine are decomposed by heating them in a platinum crucible with strong sulphuric acid, the heat being continued till all the

* Edinb. Phil. J. liii. 356.

† Chem. Gaz. 1850, 366.

‡ Chem. Soc. Qu. J. v. 151.

§ Compt. rend. xxxviii. 393; xl. 966.

‖ Ibid. xxxviii. 393.

fluorine is expelled in the form of hydrofluoric acid, and the excess of sulphuric acid is likewise drawn off. The residual sulphate is then weighed, and the quantity of metal in it calculated; this quantity deducted from the original weight of the fluorine gives the quantity of fluorine. Or, supposing no other volatile acid to be present, if the difference in the weight of the fluoride and the sulphate formed from it be *d*, the quantity of fluorine may be found by means of the equations,

$$SO_4 - F = d; \quad \frac{SO_4}{F} = \frac{48}{18 \cdot 7}.$$

The second mode of calculation is equally applicable, whether the fluorine be combined with one metal or with several.

Fluorides frequently occur in nature in conjunction with phosphates, as in apatite and in bones. To analyse such a compound, it is first heated with sulphuric acid to expel the fluorine; the residue digested with alcohol to dissolve the phosphoric acid which has been set free; the quantity of that acid determined by precipitation with ammonia and sulphate of magnesia; and the metals now remaining in the form of sulphates determined by methods already given. Lastly, the total weight of these metals, together with that of the phosphoric acid, or rather of the corresponding salt-radical (PO_8, if the phosphates are tribasic), is deducted from the original weight of the mineral; and the difference gives the quantity of fluorine.

From solutions, fluorine is generally precipitated as fluoride of calcium, from the weight of which, if pure, the quantity of fluorine may be immediately calculated; but if other substances are precipitated at the same time, the quantity of fluorine must be determined in the manner above described.

BUNSEN'S GENERAL METHOD OF VOLUMETRIC ANALYSIS.

This method, which is applicable to a great number of analyses depending upon oxidation and reduction, is founded on the principle of liberating a quantity of iodine equivalent to the substance which is to be estimated, and determining the amount of this iodine by means of a standard solution of sulphurous acid.

Iodine and sulphurous acid, in presence of water, form hydriodic and sulphuric acids;

$$SO_2 + I + HO = SO_3 + HI,$$

each equivalent of sulphurous acid thus transformed corresponding to 1 eq. of iodine, or 32 parts by weight of anhydrous sulphurous acid to 126·36 parts of iodine.

For this reaction, however, it is necessary that the liquids be very dilute; for, at a certain degree of concentration, the opposite change takes place, sulphuric and hydriodic acids decomposing each other in such a manner as to yield sulphurous acid, water, and iodine. The solution of sulphurous acid used for the estimation of iodine must never contain more than from 0·04 to 0·05 per cent. of iodine.

The method requires three standard test-liquids: a solution of iodine, a solution of sulphurous acid, and a solution of iodide of potassium. To prepare the first, a weighed quantity of iodine, as pure as can be obtained, is dissolved in a concentrated solution of iodide of potassium (which must be perfectly free from free iodine and iodate of potash, and therefore must not exhibit any brown colour, either by itself or on addition of hydrochloric acid), and the liquid diluted to such a degree that 200 cubic centimeters may contain 1 gramme of iodine, so that, if a division of the burette contains half a cubic centimeter, each degree may contain $\frac{1}{400}$ or 0·0025 of a gramme of the iodine used. But as commercial iodine, even the purest, contains traces of chlorine, it is necessary to de-

termine the real value in iodine of a degree of the burette by special experiment. The method of doing this will be presently described (p. 727).

Of the second test-liquid, the dilute sulphurous acid, it is best to prepare a considerable quantity, 20 or 30 litres, at a time, so that the alteration produced in it by the oxidising action of the air during the course of an experiment, or even in a day, may be imperceptibly small. To give the acid the proper degree of solution, 20 or 30 litres of water are mixed with a small measure-glassful of concentrated sulphurous acid; the liquid shaken; 200 burette-degrees, or 100 cubic centim. of it measured off; this portion of liquid mixed with starch, and the standard solution of iodine added from the burette, till the liquid just exhibits a perceptible blue colour. If the number of burette-degrees of the iodine-solution required for this purpose be t, and the quantity of iodine in one degree be a, the quantity, x, of anhydrous sulphurous acid, $\ddot{S}$, in 100 degrees of the acid solution will be

$$x = \frac{\ddot{S}}{I} . at = \frac{32}{126{\cdot}36} . at.$$

The most convenient strength of the sulphurous acid solution is about 0·03 anhydrous sulphurous acid to 100 water.* It must be tested at the commencement of each day's work, and will require renewal after three or four days.†

The third test-liquid is a solution of pure iodide of potassium, containing about 1 grm. of the iodide to 10 cubic centimetres of water.

1. *Determination of the amount of pure Iodine in a commercial sample.*—The weighed sample is dissolved in the solution of iodide of potassium, in the proportion of about 0·1 grm. to

* As a cubic centimeter of water weighs a gramme, this is the same as 0·03 grm. in 100 cubic centimeters or 200 burette-divisions.

† A modification of this method, in which hyposulphite of soda is used instead of sulphurous acid, has been introduced by Mr. E. O. Brown. (See page 109 of this volume.)

4 or 5 cub. centim. of liquid. To the resulting brown solution, as many measures, n, of the standard-solution of sulphurous acid are added as are required to destroy the brown colour completely. The next step is to determine the quantity of iodine, x, by which this quantity of sulphurous acid has been partially decomposed. This is effected by adding three or four cubic centimeters of clear and very dilute starch-solution, and then dropping in the standard-solution of iodine from the burette, till a blue colour begins to appear. If t' degrees of the iodine-solution are required for this purpose, and the quantity of iodine in each degree is a, the quantity required to decompose completely the n measures of sulphurous acid is $x + at'$. Further, if we determine the quantity of iodine, $a\,t$, required to decompose one measure of the sulphurous acid solution, we shall obtain the equation $x + at' = nat$; whence

$$x = a\,(nt - t').$$

If the weight of the sample of iodine be A, the quantity expressed as a percentage will be $\frac{100\,a}{A}\ (nt - t')$; and if $\frac{100\ a}{A} = 1$, that is, if the quantity weighed out is exactly $100\ a$ (4 grms. if $a = \frac{1}{400}$ grm.), the difference of the two measurements, $nt - t'$, gives at once the per centage of iodine in the sample.

The same method may be applied to determine the quantity of free iodine contained in any liquid.

2. *Determination of Chlorine.*—Chlorine decomposes a solution of iodide of potassium instantly and completely, without the aid of heat, setting free an equivalent quantity of iodine. If this quantity of liberated iodine be determined in the manner just described, the quantity of chlorine will be given by the equation,

$$x = \frac{\mathrm{Cl}}{\mathrm{I}}\ a\,(nt - t').$$

3. Similarly for *Bromine:*

$$x = \frac{\mathrm{Br}}{\mathrm{I}} \cdot a\,(nt - t').$$

4. *Chlorine and Bromine together.*—To estimate the quantity of chlorine contained in a sample of bromine, a quantity A of the bromine, thoroughly dried, is dissolved in a solution of iodide of potassium, and the quantity of iodine, $a\,(nt - t')$ thereby separated, is determined as above. Then, denoting the quantity of bromine by x, and that of chlorine by y, we have the equations:—

$$x + y = A;$$

$$\frac{\mathrm{I}}{\mathrm{Br}}\,x + \frac{\mathrm{I}}{\mathrm{Cl}}\,y = a\,(nt - t');$$

whence $$x = \frac{\frac{\mathrm{I}}{\mathrm{Cl}}\,A - a\,(nt - t')}{\frac{\mathrm{I}}{\mathrm{Cl}} - \frac{\mathrm{I}}{\mathrm{Br}}};\ y = \frac{a\,(nt - t') - \frac{\mathrm{I}}{\mathrm{Br}}\,A}{\frac{\mathrm{I}}{\mathrm{Cl}} - \frac{\mathrm{I}}{\mathrm{Br}}}.$$

If the chlorine and bromine are in a state of combination, they may be set free by distilling the mixture or compound with bichromate of potash and sulphuric acid, the evolved gases being passed into the solution of iodide of potassium.

A similar method may be applied to a mixture of chlorine and iodine, the equations then becoming—

$$x + y = A;\quad \frac{\mathrm{I}}{\mathrm{Cl}}\,x + y = a\,(nt - t').$$

5. *Chlorites and Hypochlorites.*—A solution of the salt is mixed with solution of iodide of potassium, and hydrochloric acid added in slight excess. From the quantity of iodine, $a\,(nt-t')$ thus separated, the quantity of chlorous acid x', or hypochlorous acid x'', may be determined from the equations

$$x' = \frac{\dddot{\mathrm{Cl}}}{4\mathrm{I}}\,a\,(nt - t')$$

$$x'' = \frac{\dot{\mathrm{Cl}}}{2\mathrm{I}}\,a\,(nt - t')$$

It must be remembered that 1 eq. ClO decomposes 2 eq. KI, and 1 eq. ClO_3 decomposes $4KI$.

This method is well adapted to the estimation of chloride of lime for commercial purposes. If A be the weight of the sample, the percentage of chlorine will be $\frac{100\ \mathrm{Cl}}{A\,.\,\mathrm{I}}\,a\,(nt - t')$; and if A be equal to $\frac{100\ \mathrm{Cl}}{\mathrm{I}}\,a$, the difference of the two measurements, $nt - t'$, gives directly the bleaching power of the product in percentage of chlorine.

6. *Chromates.* — When a chromate, *e. g.* bichromate of potash, is boiled with excess of fuming hydrochloric acid, every 2 eq. chromic acid eliminate 3 eq. chlorine:—

$$2CrO_3 + 6HCl = Cr_2Cl_3 + 6HO + 3Cl;$$

and the 3 eq. of chlorine passed into a solution of iodide of potassium, liberate 3 eq. of iodine, which may be estimated volumetrically as above. Hence the quantity x of chromic acid contained in a known weight A of bichromate of potash, or any other chromate, will be given by the equation—

$$x = \frac{2\ \dddot{\mathrm{Cr}}}{3\ \mathrm{I}}\,a\,(nt - t');$$

$$\text{or in 100 parts: } x = \frac{200\ \dddot{\mathrm{Cr}}}{A\,.\,3\mathrm{I}}\,a\,(nt - t').$$

If $A = \frac{200\ \dddot{\mathrm{Cr}}}{3\ \mathrm{I}}\,a$, that is, if the sample taken weighs exactly this quantity, the difference of the two measurements, $nt - t'$, gives directly the percentage of chromic acid. Similarly, for $A = 100\,\frac{\dot{\mathrm{K}} + 2\dddot{\mathrm{Cr}}}{3\mathrm{I}}\,a$, this difference would give the percentage of pure bichromate of potash, and for $A = 200\,\frac{\mathrm{Pb} + \dddot{\mathrm{Cr}}}{3\mathrm{I}}\,a$, the percentage of pure chromate of lead in these respective salts.

The analysis is made by introducing a weighed quantity of the chromate into a small flask holding about 40 cubic centimeters, filled about two-thirds with fuming hydrochloric acid, and having a gas-delivery tube adapted to its neck by means of a tube of vulcanised caoutchouc. The glass tube is inserted into the neck of an inverted retort, of the capacity of about 160 cubic centim., containing a solution of iodide of potassium. The middle of the neck of the retort is blown out into a bulb to receive any liquid that may be thrown up. A piece of vulcanised caoutchouc is tied tightly over the open end of the glass tube, and a slit cut in it with a sharp, wet penknife. This slit opens when pressed from within, but closes tightly when pressed in the opposite direction, thus forming an excellent valve. The liquid in the flask is now boiled for three or four minutes, by which time the whole of the chlorine is expelled, and an equivalent quantity of iodine liberated.

The volumetric analysis of pure bichromate of potash affords an easy method of determining the value of a, or the quantity of pure iodine contained in a burette degree of the standard solution (p. 723). For if the bichromate of potash be pure, its weight A is exactly equal to $\frac{\dot{K} + 2\,\dddot{Cr}}{3I}\,a\,(nt - t')$; therefore,

$$a = \frac{3IA}{(\dot{K} + 2\,\dddot{Cr})\,(nt - t')}.$$

7. *Peroxides.*—The quantity of oxygen in the peroxides of lead, manganese, &c., may be estimated in a similar manner to chromic acid. Thus, the percentage of oxygen in binoxide of lead PbO_2 is given by the formula—

$$x = 100\,\frac{2O}{A \cdot I}\,a\,(nt - t');$$

and the percentage of pure binoxide of manganese in a commercial sample of the black oxide by the formula —

$$x = \frac{100\ \ddot{\mathrm{M}}\mathrm{n}}{A\ .\ \mathrm{I}}\ a\,(nt - t').$$

Besides the preceding and a great number of other bodies which give rise to a separation of free chlorine, the iodometric method may be applied to the estimation of substances which are raised by chlorine to a higher degree of oxidation. These substances are heated with fuming hydrochloric acid and a known weight, *p*, of pure bichromate of potash; the evolved chlorine is passed into iodide of potassium; and the liberated iodine estimated as above. The quantity thus separated, viz. $a\ (nt - t')$, is equal to the quantity of iodine, $\frac{p\ .\ 3\mathrm{I}}{\dot{\mathrm{K}} + 2\dddot{\mathrm{C}}\mathrm{r}}$, equivalent to the bichromate used *minus* the quantity *i*, equivalent to the protoxide to be estimated. The latter is therefore,

$$i = \frac{p\ .\ 3\mathrm{I}}{\dot{\mathrm{K}} + 2\dddot{\mathrm{C}}\mathrm{r}} - a\,(nt - t').$$

Thus, to determine the amount of protoxide of iron in a given sample of iron-ore, it must be remembered that each equivalent of iodine or chlorine converts 2 eq. of the protoxide into sesquioxide:—

$$2\mathrm{FeO} + \mathrm{I} + \mathrm{HO} = \mathrm{Fe_2O_3} + \mathrm{HI}.$$

If then *i* be the quantity of iodine required to convert the protoxide of iron in a given sample into sesquioxide, the quantity *e* of protoxide in this sample will be $e = i\ .\ \frac{2\dot{\mathrm{F}}\mathrm{e}}{\mathrm{I}}$; and substituting for *i* its value above given, we have

$$e = \frac{6\ \dot{\mathrm{F}}\mathrm{e}}{\dot{\mathrm{K}} + 2\dddot{\mathrm{C}}\mathrm{r}}\,p - \frac{2\ \dot{\mathrm{F}}\mathrm{e}}{\mathrm{I}}\ a\,(nt - t');$$

and hence it is easy to calculate the equivalent quantities of metallic iron and sesquioxide.

Various other applications of the method, will be found in Professor Bunsen's memoir.*

METALS OF THE ALKALIES AND EARTHS.

POTASSIUM.

Preparation of Potassium.—The process of obtaining this metal by igniting a mixture of carbonate of potash and charcoal, has received considerable improvements from the researches of Maresca and Donny.† The ordinary form of the process, which is that devised by Brunner, is dangerous, and gives very uncertain results, the quantity of metal obtained by it being often very small, and sometimes, even when the greatest care is taken, absolutely nothing. The danger arises from the obstruction of the connecting tube by the black substance formed by the action of carbonic oxide on the potassium there deposited; and the loss of product is due, partly to the formation of this black substance, and partly to the escape of portions of the metal in the form of vapour. The first of these inconveniences can only be obviated by keeping the entire length of the connecting tube at a red heat during the whole operation. But in that case, if the large receivers invented by Brunner (see figures 152, 153, p. 521, Vol. I.) are used, not a particle of the metal condenses, the whole escaping in the form of vapour. Hence it is necessary to use much smaller receivers; and the form which the authors

* Ann. Ch. Pharm. lxxxvi. 265; Chem. Soc. Qu. J. viii. 218.

† Ann. Ch. Phys. [3], xxxv. 147.

find to give the best results, is that of a shallow rectangular box, 12 centimeters long, 6 wide and 4 deep. Another source of failure in the operation is the want of a due proportion between the carbonate of potash and charcoal in the calcined tartar. To obtain the best result, the quantity of charcoal should be neither more nor less than that which is theoretically required for the complete reduction of the potash present. Whether this is the case, can only be ascertained by a previous analysis of the burnt tartar; and any excess or deficiency of charcoal, must be remedied by mixing samples of tartar of different qualities. Lastly, to prevent the perforation of the iron bottle during the ignition, it should be coated, not with clay luting, but with fused borax. Such a coating is easily formed by sprinkling pulverised borax on the bottle when it is at a dull red heat.

Preparation of Potassium by Electrolysis. — A mixture of 1 at. chloride of potassium and 1 at. chloride of calcium (which mixture is used because it melts at a much lower temperature than chloride of potassium alone), is melted in a small porcelain crucible over a lamp, and subjected to the action of a Bunsen's battery of six elements with carbon poles, the heat being so regulated that a solid crust forms round the negative carbon pole, while the mixture remains fused and allows the free evolution of chlorine at the positive pole. When the decomposition has been continued in this manner for about twenty minutes, and the cooled crucible is opened under rock-oil, a large quantity of potassium, almost chemically pure, is generally obtained. If the same experiment be repeated at a white heat over a charcoal fire, with an iron wire as negative pole, small globules of potassium are seen burning on the surface; and these when analysed, are found to be almost pure. (Matthiessen.*)

Preparation of pure Hydrate of Potash. — Wöhler recommends for this purpose the decomposition of pure nitre by

* Chem. Soc. Qu. J. viii. 30.

metallic copper at a red heat. 1 pt. of nitre and 2 or 3 pts. of thin copper plate cut into small pieces, are arranged in alternate thin layers in a covered copper crucible, and exposed for half an hour to a moderate red heat. The cooled mass is then treated with water, the liquid left to stand in a tall covered cylindrical vessel till the oxide of copper has completely settled down, and the pure solution of potash then decanted with a siphon.

With the above proportions of nitre and copper part of the latter is converted only into suboxide. It may, therefore, be used for a second preparation of potash, by mixing 1 pt. of it with 1 pt. of nitre and 1 pt. of metallic copper.

Iron may also be used to decompose the nitre; but the potash thereby obtained is contaminated with small quantities of carbonic acid, silica, &c. The same objection applies to the use of an iron crucible, if a perfectly pure product be required.*

Estimation of Potassium. — Potassium, when it occurs in a compound not containing any other metal, may be estimated either as sulphate or as chloride. All potassium-salts containing volatile acids, are decomposed by heating them with sulphuric acid, the excess of which may afterwards be expelled by a stronger heat, and the quantity of potassium or potash calculated from the weight of the residual neutral sulphate. It is difficult, however, to expel the last traces of free sulphuric acid by mere ignition; but they may be completely driven off by dropping a lump of carbonate of ammonia into the crucible, and repeating the ignition with the cover on; the sulphuric acid then diffuses into the atmosphere of ammonia in the crucible, and a perfectly neutral sulphate remains. It contains 54·06 per cent. of potash, KO.

In estimating potassium as chloride, the only precaution to be observed is to ignite the chloride in a covered crucible,

* Ann. Ch. Pharm. lxxxvii. 373.

as, when strongly heated in contact with the air, a portion of it volatilises. The chloride contains 52·47 per cent. of potassium, equivalent to 63·19 per cent. of potash.

The separation of potassium from all soluble substances except ammonia, is easily effected by precipitating it with bichloride of platinum, adding alcohol to complete the precipitation of the chloroplatinate of potassium, collecting the precipitate on a weighed filter, washing with alcohol, and drying it at 100° C. It contains 16·04 per cent. of potassium equivalent to 19·31 of potash.

SODIUM.

Preparation.—Deville finds that the reduction of this metal from the carbonate, by ignition with charcoal, is greatly facilitated by the addition of some substance, such as chalk, which retains the mass in a pasty state during ignition. The best product is obtained with a mixture of 717 pts. of dry carbonate of soda, 175 charcoal, and 108 chalk. With regard to the form of apparatus, and the mode of conducting the process, Deville follows exactly the directions given by Maresca and Donny (p. 729), for the preparation of potassium.*

Sodium may be readily obtained by electrolysis, in a manner similar to that described for potassium (p. 730), using, however, a mixture of 1 at. chloride of sodium, and 2 at. chloride of calcium. (Matthiessen.)

Carbonate of Soda.—Solutions of carbonate of soda are capable of assuming the state of supersaturation, and exhibiting phenomena similar to those of the sulphate (I. 555). An aqueous solution of the salt, saturated at a high temperature, and enclosed while boiling hot in sealed tubes or well-corked flasks, remains supersaturated at ordinary temperatures,

* Ann. Ch. Phys. [3], xliii. 5.

and frequently, even when cooled several degrees below 0° C., not depositing any crystals. Keeping the air in contact with the liquid from agitation (as by covering the hot solution with a glass receiver), is often sufficient to prevent the formation of crystals at ordinary temperatures; but free access of air causes immediate solidification, attended with rise of temperature. The passage of an electric current through a supersaturated solution, does not induce any change of state.

The supersaturated solutions of carbonate of soda contain a salt having less water of crystallisation than the ordinary 10-hydrated salt. The salt contained in them is, in fact, a 7-hydrated salt, $NaO . CO_2 + 7HO$, and of this salt there are two modifications, differing in crystalline form and in degree of solubility. One of them (*a*) crystallises in rhombohedral crystals; the other (*b*), in square tables or low prisms: both these salts absorb water rapidly. The salt *b* was first obtained by Thomson, who, however, supposed it to contain 8 at. water. When a solution saturated at the boiling heat, and containing a slight excess of the solid salt, is enclosed in a flask, which is corked immediately after the boiling has ceased, no crystals are deposited from it for a long time on cooling down to between 25° and 18° C.; but on cooling below 8°, it deposits chiefly the salt *b*. When cooled to between 16° and 10°, it yields the salt *a*, which redissolves between 21° and 22°, forms again on cooling to 19°; and on cooling from 10° to 4°, becomes opaque, and passes into the salt *b*. After cooling to a lower temperature, and for a longer time, when the state of supersaturation ceases, the whole is converted into a mass of crystals of the ordinary salt $NaO . CO_2 + 10$ aq. The following table gives a comparative view of the quantities of the 10-hydrated and of the two varieties of the 7-hydrated salt, contained in 100 parts of the saturated solutions at different temperatures:—

Temperature	0°	10°	15°	20°	25°	30°	38°	104°.
10-hydrated salt	7·0	12·1	16·2	21·7	28·5	37·2	51·7	45·5
7-hydrated (*b*)	20·4	26·3	29·6	38·6	38·1	43·5	—	—
7-hydrated (*a*)	31·9	37·9	41·6	45·8	—	—	—	—

Hence it appears, that carbonate of soda exhibits a maximum of solubility, at 38° C. The decrease of solubility above this point arises from the formation of another hydrate, $NaO . CO_2 + HO$. This hydrate, which separates out when a solution saturated at 104° C. is concentrated by boiling, is more soluble in cold than in hot water, and the crystals which have been separated by boiling, redissolve in the mother liquor, when left to cool in a closed vessel. (H. Loewel.*)

Besides the hydrates above-mentioned, two others have been discovered by Jacquelain †, viz. $NaO . CO_2 + 15HO$, which crystallises below − 20°, and when dried in vacuo gives off 5 atoms of water, and is converted into the ordinary ten-hydrated salt; and $NaO . CO_2 + 9HO$, obtained by repeatedly crystallising a solution which at first contains a portion of bicarbonate of soda. Jacquelain also finds that carbonate of soda gives off carbonic acid when melted, even in a stream of pure and dry carbonic acid.

Sulphate of Soda.—This salt appears to be capable of existing in solution in three different states, viz. as anhydrous salt, $NaO . SO_3$, as the seven-hydrated salt, $NaO . SO_3 + 7HO$, and as the ten-hydrated salt, $NaO . SO_3 + 10HO$, which is the ordinary Glauber's salt. The following table shows the solubility (as determined by Loewel ‡) of the anhydrous salt, and of the two hydrates, in water, at various temperatures; also the quantity of anhydrous salt corresponding in each case to the hydrate dissolved. The numbers in the table are the quantities of salt dissolved in 100 parts of water.

* Ann. Ch. Phys. [3], xxxiii. 334.
† Compt. rend. xxx. 106.
‡ Ann. Ch. Phys. [3], xlix. 32.

SOLUBILITY OF SULPHATE OF SODA.

Temp.	$NaO.SO_3$,	$NaO.SO_3+10HO$.		$NaO.SO_3+7HO$.	
	Anhydrous.	Anhydrous.	Hydrate.	Anhydrous.	Hydrate.
0° C.	. .	5·02	12·16	19·62	44·84
10	. .	9·00	23·04	30·49	78·90
15	. .	13·20	35·96	37·43	105·79
18	52·25	16·80	48·41	41·63	124·59
20	52·76	19·40	58·35	44·73	140·01
25	51·53	28·00	98·48	52·94	188·46
26	51·31	30·00	109·81	54·07	202·61
30	50·37	40·00	184·09		
33	49·71	50·76	323·13		
34	49·53	55·00	412·22		
40·15	48·78				
50·40	46·82				
59·79	45·42				
70·61	44·35				
84·42	42·96				
103·17	42·65				

Sulphate of Soda and Potash. — Gladstone* has obtained a salt containing $\left.\begin{matrix}5\,KO\\NaO\end{matrix}\right\}6SO_3$, by fusing the neutral or acid sulphate of potash with chloride of sodium, or sulphate of potash with sulphate of soda, dissolving the fused mass in hot water, and leaving it to crystallise, or by mixing the two salts in hot aqueous solution. The salt which crystallised out was anhydrous, and exhibited the crystalline form of sulphate of potash. H. Rose† had previously obtained the same salt, but had not assured himself of its definite constitution.

Estimation of Sodium.—This metal, like potassium, may be estimated either as chloride or as sulphate. The sulphate contains 32·54, and the chloride 39·53 per cent. of sodium.

Sodium is separated from potassium by means of bichloride of platinum, with addition of alcohol, which precipitates the potassium, and leaves the sodium in solution. The quantity of potassium may then be determined from the weight of the

* Chem. Soc. Qu. J. vi. 106.

† Pogg. Ann. lii. 452.

precipitate, and the sodium estimated by difference. Or if a direct estimation of the sodium be desired, the filtered liquid may be freed from excess of platinum by means of hydrosulphuric acid, and the sodium in the filtrate, which then contains no other metal, determined as sulphate.

If the potassium and sodium are in the form of chlorides, the method just described may be applied immediately; if not, it is best first to convert them into chlorides, which may in some cases be done by merely heating the mixed salts with excess of hydrochloric acid, or, in case of sulphuric or phosphoric acid being present, by precipitating the acid with chloride of barium, removing the excess of barium with carbonate of ammonia, and expelling the ammoniacal salts from the filtrate by evaporation and ignition. The residue is a mixture of the chlorides of potassium and sodium.

AMMONIUM.

A compound radical consisting of ammonia with an additional atom of hydrogen, was first supposed to exist in the ordinary salts of ammonia by Berzelius, and termed ammonium. This body has never been insulated, but is supposed to appear, in a certain experiment, in combination with mercury, and possessed of the metallic character (I. 203). The compounds of ammonium are always strictly isomorphous with the corresponding compounds of potassium.

Chloride of ammonium, Hydrochlorate or Muriate of ammonia, Sal-ammoniac, $NH_4 . Cl$.—This salt is formed when ammonia is neutralised by hydrochloric acid; $NH_3 + HCl = NH_4 . Cl$. It is prepared in large quantity from the ammoniacal liquor obtained in the distillation of bones, in the manufacture of animal charcoal, and from the liquor which condenses in the distillation of coal for gas. These liquors contain ammonia principally in the state of carbonate and hydrosulphate, which may be converted into chloride of ammonium by the

addition of hydrochloric acid. The salt is purified by crystallisation, and sublimed in vessels of iron or earthenware, in the upper part of which it condenses and forms a solid cake, the condition in which sal ammoniac is always met with in commerce.

Sal-ammoniac is tenacious and difficult to reduce to powder; its sp. gr. is 1·45. It has a sharp and acrid taste, and dissolves in 2·72 parts of cold, and in an equal weight of boiling water; it is also soluble in alcohol. It generally crystallises from solution in feathery crystals, which are formed of rows of minute octohedrons attached by their extremities. At a red heat it volatilises without previous fusion.

A corresponding bromide, iodide, and fluoride of ammonium may be formed by neutralising ammonia with hydrobromic, hydriodic, and hydrofluoric acids.

Sulphides of Ammonium.—When 4 volumes of ammonia combine with 2 of hydrosulphuric acid gas, the sulphide of ammonium is produced; $NH_3 + HS = NH_4 . S$. Ammonium combines with sulphur in several other proportions, which are obtained on mixing and distilling the various sulphides of potassium with sal ammoniac. In the reciprocal decomposition which occurs, the potassium combines simply with chlorine, and the ammonium with sulphur. The following compounds are generally enumerated: $NH_4 . S$; $NH_4 . S + HS$; $NH_4 . S_3$ and $NH_4 . S_5$. The protosulphide has long been formed by distilling a mixture of quicklime, sulphur, and sal ammoniac, and known under the name of the *fuming liquor of Boyle.* It is a volatile liquid, the vapour of which is decomposed by oxygen, and thus fumes produced. The second compound, which is a sulphide of hydrogen and ammonium, is formed by transmitting hydrosulphuric acid gas through solution of ammonia to saturation. This liquid is generally called the hydrosulphate of ammonia, and is a very useful reagent in chemical analysis. All the sulphides of ammonium are soluble in water and alcohol without decomposition.

Nitrate of ammonium, $NH_4O . NO_5$.—When nitric acid is saturated with ammonia, a salt is obtained which crystallises in six-sided prisms, and is isomorphous with nitrate of potash. Besides the elements of anhydrous nitric acid and ammonia, this salt contains an atom of water which cannot be separated from it, which is also found in, and is equally essential to, the salts formed by neutralising all other oxygen-acids by ammonia, such as sulphurous acid, sulphuric, carbonic, &c., in contact with water. The hydrogen of this water is assigned to the ammonia, to form ammonium, which the oxygen converts into oxide of ammonium; so that the product is nitrate of the oxide of ammonium; or $NH_3 + HO . NO_5 = NH_4O . NO_5$. This salt deflagrates with flame when thrown upon red-hot coals. When decomposed between 300° and 400°, it is resolved into water and nitrous oxide (I. 339).

Carbonates of Ammonium.—The neutral carbonate of oxide of ammonium appears not to exist in the free state, but by distilling the sesquicarbonate of ammonia of the shops at a gentle heat, Rose obtained a volatile crystalline salt, which may be viewed as a compound of anhydrous carbonate of ammonia with carbonate of ammonium: $NH_3 . CO_2 + NH_4O . CO_2$. When the commercial salt is exposed to the air, it loses its pungent odour, and a white friable mass remains, which is the bicarbonate of ammonium, or carbonate of water and oxide of ammonium: $HO . CO_2 + NH_4O . CO_2$. This is a stable salt, and may be dissolved and crystallised without change.

The sesquicarbonate of ammonia of the shops is a crystalline transparent mass, which Rose finds to have generally, but not always, the composition assigned to it by Mr. Phillips, or to contain $3CO_2$ with $2NH_3$ and 2HO. Rose is disposed to consider it a compound of anhydrous carbonate of ammonia and bicarbonate of oxide of ammonium, or $NH_3CO_2 + (HO . CO_2 + NH_4O . CO_2)$. Mr. Scanlan has shown that a small quantity of water dissolves out the carbonate from this

salt, and leaves the bicarbonate, which is the least soluble. This observation does not prove the commercial salt to be a mechanical mixture of the two salts derived from it, as many undoubted compounds of two salts are decomposed by water, when one of the constituent salts is much more soluble than the other. Another salt was obtained by Rose, in well-formed crystals, of which the ammonia and carbonic acid are in the proportions of the sesquicarbonate, but with three additional atoms of water. No fewer than twelve different carbonates of ammonia are described by that chemist.*

Sulphate of Ammonium, $NH_4O \cdot SO_3 + HO$.—This is a highly soluble salt, which possesses an atom of water of crystallisation, in addition to the atom which is essential to its constitution. It appears also to crystallise without this water.

Phosphates of Ammonium. — The biammoniacal tribasic phosphate, $(2NH_4O \cdot HO) \cdot PO_5$, analogous to ordinary phosphate of soda, is obtained by decomposing the acid phosphate of lime with carbonate of ammonium. It forms large transparent crystals, belonging to the oblique prismatic system, which effloresce on the surface when exposed to the air, and give off a portion of their ammonia, even at ordinary temperatures. The salt dissolves in 4 parts of cold, and a smaller quantity of hot water. (Mitscherlich.)

The monoammoniacal phosphate, $(NH_4O \cdot 2HO) \cdot PO_5$, is formed by adding phosphoric acid to the solution of the preceding salt, till the liquid becomes slightly acid. It forms crystals belonging to the square prismatic system, and somewhat less soluble than the preceding. (Mitscherlich.)

A basic phosphate is also formed by mixing a concentrated solution of the biammoniacal salt with ammonia; but it quickly gives off ammonia, and is reconverted into the biammoniacal salt.

* Scientific Memoirs, ii. 98.

Pyrophosphate and *Metaphosphate of Ammonium* may also be formed by adding ammonia to the aqueous solutions of the respective acids; but they are converted by evaporation into the corresponding tribasic phosphates. (Graham.)

Oxalates of Ammonium.—The neutral oxalate, $C_4(NH_4)_2O_8$ (regarding oxalic acid as a bibasic acid, p. 539), is obtained by neutralising the aqueous acid with ammonia. It crystallises in long prisms united in tufts and belonging to the right-prismatic system: they contain 2 eq. of water, which they give off at a moderate heat. The acid oxalate, $C_4(H \cdot NH_4)O_8$, is precipitated in the crystalline form, when the solution of the neutral salt is mixed with oxalic, sulphuric, or hydrochloric acid. It is much less soluble than the neutral salt.

A superoxalate, $C_4(H \cdot NH_4)O_8 + C_4H_2O_8$, separates from a solution of equal parts of oxalic acid and the acid oxalate, in crystals resembling those of the preceding salt, and containing 4 eq. of water.

Neutral oxalate of ammonium, when strongly heated, gives off 4 at. water, and yields a sublimate of oxamide (p. 558):

$$\underbrace{C_4N_2H_8O_8}_{\substack{\text{Neutral oxalate}\\ \text{of ammonium.}}} - 4HO = \underbrace{C_4N_2H_4O_4}_{\text{Oxamide.}}.$$

The acid salt, when heated, gives off 2 at. water, and leaves oxamic acid (p. 542):

$$\underbrace{C_4NH_5O_8}_{\substack{\text{Acid oxalate of}\\ \text{ammonium.}}} - 2HO = \underbrace{C_4NH_3O_6}_{\text{Oxamic acid.}}.$$

All amides and amidogen-acids may, indeed, be regarded as ammonium-salts *minus* water. But few of them, however, are produced by the actual abstraction of water from the corresponding ammonium-salts; they are more generally produced by the action of ammonia on anhydrous acids, acid chlorides, or compound ethers (pp. 542, 557, 561).

The compounds formed by the action of dry ammonia on the anhydrous acids, sometimes called anhydrous salts of ammonia, and, by H. Rose, *ammon-salts*, are all either amides or amidogen-acids. Thus, 2 vols. ammoniacal gas, and 1 vol. carbonic acid, unite and form the compound NH_3CO_2, which, doubling the atomic weight, is *carbamide*, $N_2\left\{\begin{matrix}C_2O_2\\H_4\end{matrix}\right.$, or 2 at. ammonia in which one-third of the hydrogen is replaced by the biatomic radical carbonyl, C_2O_2. With anhydrous sulphuric acid, ammonia forms two compounds, viz. NH_3SO_3, Rose's *sulph-atammon*, or *sulphamide*, $= N_2\left\{\begin{matrix}S_2O_4\\H_4\end{matrix}\right. + 2HO$; and *sulphamic acid*, $NH_3S_2O_6 = \left.\begin{matrix}N.\overbrace{H_2(S_2O_4)}\\H\end{matrix}\right\}O_2$. Similarly, with anhydrous sulphurous acid, ammonia forms thionamide, $NH_3SO_2 = N_2\left\{\begin{matrix}S_2O_2\\H_4\end{matrix}\right.$, and thionamic acid, $NH_3S_2O_6 = \left.\begin{matrix}N.\overbrace{H_2(S_2O_2)}\\H\end{matrix}\right\}O_2$. [For the amides of phosphoric acid, see page 695.]

All salts of ammonium, heated with fixed caustic alkalies, give off ammonia, which may be absorbed by hydrochloric acid, and its quantity then determined either by evaporating the solution of chloride of ammonium over the water-bath, or, more exactly, by precipitation with bichloride of platinum (p. 385).

LITHIUM.

Preparation.—Pure chloride of lithium is fused over a spirit-lamp, in a small porcelain crucible, and decomposed by a zinc-carbon battery of four or six cells. The positive pole is a small splinter of gas-coke (the hard carbon deposited in the gas-retorts), and the negative pole an iron wire about

the thickness of a knitting-needle.* After a few seconds, a small silver-white regulus is formed under the fused chloride, round the iron wire and adhering to it, and after two or three minutes attains the size of a small pea. To obtain the metal, the wire pole and regulus are lifted out of the fused mass, by a small, flat, spoon-shaped iron spatula. The wire may then be withdrawn from the still melted metal, which is protected from oxidation by a coating of chloride of lithium. The metal may now be easily removed from the spatula with a pen-knife, after having been cooled under rock-oil. These operations may be repeated every three minutes; and thus an ounce of the chloride may be reduced in a very short time.

Lithium, on a freshly-cut surface, has the colour of silver, but quickly tarnishes on exposure to the air, becoming slightly yellow. It melts at 180° C. (356° F.), and if pressed at that temperature between two glass plates, exhibits the colour and brightness of polished silver. It is harder than potassium or sodium, but softer than lead, and may, like that metal, be drawn out into wire. It tears much more easily than a lead wire of the same dimensions. It may be welded by pressure at ordinary temperatures. It swims on rock-oil, and is the lightest of all known solids, its specific gravity being only 0·5986. Taking the atomic weight at 6·5, its atomic volume is therefore 1·06, being nearly the same as that of calcium.

Lithium is much less oxidable than potassium or sodium. It makes a lead-grey streak on paper. It ignites at a temperature much higher than its melting point, burning quietly, and with an intense white light. It burns when heated in

* The decomposing power of an electric current depends chiefly upon its *density*, *i. e.* upon the quotient obtained by dividing the strength of the current by the surface of the pole at which the electrolysis takes place. Thus, a current of constant strength passed through an aqueous solution of terchloride of chromium, eliminates, as its density is successively diminished (or the cross-section of the reducing pole increased), metallic chromium, chromous oxide, chromic oxide, and, lastly, hydrogen. (Bunsen, *Pogg. Ann.* xci. 619.)

oxygen, chlorine, bromine, iodine, or dry carbonic acid, and with great brilliancy on boiling sulphur. When thrown on water, it oxidises, but does not fuse like sodium. Nitric acid acts on it so violently, that it melts and often takes fire. Strong sulphuric acid attacks it slowly; dilute sulphuric acid and hydrochloric acid, quickly. Silica, glass, and porcelain are attacked by lithium at temperatures even below 200° C. (Bunsen.*)

According to Dr. Mallett †, the atomic weight of lithium is 6·95; and accordingly that of sodium is exactly the mean between those of lithium and potassium.

Nitrate of Lithia.—This salt has a strong tendency to form supersaturated solutions. Above 10° or 15° C., it crystallises in rhombic prisms, resembling those of common nitre, but below 10° in rhombohedrons; both kinds of crystals are deliquescent. The crystals which separate from the supersaturated solution at 1° C. are slender needles. (Kremers.‡)

Phosphate of Lithia. — According to W. Mayer §, the precipitate formed on adding phosphate of soda to the solution of a lithia-salt, is not a double phosphate of lithia and soda, as commonly supposed, but a tribasic phosphate of lithia, $3LiO.PO_5$. The same precipitate is also produced when a lithia-salt is treated with phosphate of potash or phosphate of ammonia, mixed with free alkali.

Estimation of Lithium.—This element, when separated from other metals, may be estimated in the form of sulphate or chloride, in the same manner as potassium or sodium. From potassium it is separated by precipitating the latter with bichloride of platinum; and from sodium, by converting the two bases into chlorides, and treating the dried chlorides, in a well-closed bottle, with a mixture of absolute alcohol and ether, which, after a few days, dissolves the whole of the chloride of lithium, and leaves the chloride of sodium undissolved.

* Ann. Ch. Pharm. xciv. 107; Chem. Soc. Qu. J. viii. 143.
† Sill. Ann. J. [2], xxii. 349.
‡ Pogg. Ann. xcii. 520.
§ Ann. Ch. Pharm. xcviii. 193.

BARIUM.

Bunsen has obtained this metal by subjecting chloride of barium, mixed up to a paste with water and a little hydrochloric acid, at a temperature of 100° C., to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner, the metal is obtained as a solid, silver-white, highly-crystalline amalgam, which, when placed in a little boat made of thoroughly ignited charcoal, and heated in a stream of hydrogen, yields barium in the form of a tumefied mass, darkly tarnished on the surface, but often exhibiting a silver-white lustre in the cavities.* Matthiessen has obtained barium by a method similar to that adopted for strontium (p. 756), but only in the form of a metallic powder.

Binoxide or Peroxide of Barium.—A solution of this oxide in dilute hydrochloric acid acts as a reducing agent on various metallic oxides, a portion of its oxygen uniting, at the moment of separation, with the oxygen of the other metallic oxide (p. 517). When peroxide of barium is introduced into a solution of bichromate of potash acidulated with hydrochloric acid, oxygen is abundantly evolved (its evolution being, however, preceded, in the case of cold dilute solutions, by the formation of a blue compound, first observed by Barreswil, and supposed by him to be a perchromic acid, Cr_2O_7); and according to Brodie's experiments, the reaction, when a great excess of bichromate of potash is present, takes place as shown by the equation,

$$2CrO_3 + 4BaO_2 = Cr_2O_3 + 7O + 4BaO,$$

the chromic acid being reduced to sesquioxide of chromium. The quantity of oxygen evolved affords the means of calcu-

* Pogg. Ann. xci. 619.

lating the per centage of real BaO_2 in the sample used. Oxide, chloride, sulphate, or carbonate of silver introduced into an acid solution of a peroxide of barium, is partly reduced to metallic silver, the quantity of metal thus reduced being, however, always less than that which is equivalent to the oxygen which exists in the peroxide together with baryta. The quantity reduced increases with the amount of the silver compound used, and diminishes as the temperature is higher. A small quantity of the silver-compound, or of any similar substance, is capable of decomposing a large quantity of the peroxide. Iodine, on the other hand, decomposes only an equivalent quantity, according to the equation,

$$BaO_2 + I = BaI + O_2 \text{ (Brodie*)}.$$

[For the separation of oxygen from the air by first converting baryta into the peroxide, and then decomposing the latter, see p. 638.]

Peroxide of barium, heated over a large spirit-lamp in a rapid current of carbonic acid gas, becomes white-hot, and at the same time small white flames burst out from its surface, probably arising from the evolution of oxygen from the still undecomposed peroxide. A similar, but much more brilliant appearance is presented when the peroxide is heated in sulphurous acid gas. (Wöhler.†)

Carbonate of Baryta, mixed with carbonate of lime and charcoal, and heated to redness in a stream of aqueous vapour, is decomposed, and yields caustic baryta. This process is recommended by Jacquelain‡ for the preparation of caustic baryta.

According to Boussingault§, a solution of chloride of barium, mixed with the native sesquicarbonate of soda called

* Phil. Trans. 1850, 759.
† Ann. Ch. Pharm. lxxviii. 175.
‡ Ann. Ch. Phys. [3], xxxii. 421.
§ Ibid. xxix. 397.

Uras, yields a precipitate of $2BaO.3CO_2$. Laurent assigns to this precipitate the formula $2BaO.3CO_2 + HO$. H. Rose*, on the other hand, finds that chloride of barium and bicarbonate of soda always yield a precipitate consisting merely of $BaO.CO_2$, and similarly with lime.

Recently-precipitated *sulphate of baryta*, enclosed, with a solution of bicarbonate of soda, or with dilute sulphuric acid, in a sealed glass tube, and heated for 60 hours to 250° C. (472° F.), dissolves to a slight extent, and separates out on the sides of the tube in microscopic crystals, whose form agrees with that of heavy spar. Pure water or a solution of sulphide of sodium does not perceptibly dissolve sulphate of baryta under similar circumstances. (Senarmont.†)

Estimation of Barium.—Barium is almost always estimated in the form of sulphate, the precipitation and filtration being performed in the manner already described for the estimation of sulphuric acid (p. 686).

Precipitation with a soluble sulphate likewise serves to separate barium from all other metals except strontium, calcium, and lead.

Barium is also sometimes estimated as carbonate, being precipitated by carbonate of ammonia with addition of caustic ammonia, and the liquid boiled to render the precipitation complete. The carbonate is not decomposed by ignition.

STRONTIUM.

Preparation. — This metal is also obtained by the electrolysis of its chloride in the fused state. A small crucible, with a porous cell in the middle, is filled with anhydrous chloride of strontium, mixed with a little chloride of ammonium, and in such a manner that the level of the fused chloride within the cell may be much higher than in the cru-

* Pogg. Ann. lxxxvi. 293.
† Ann. Ch. Phys. [3], xxxii. 129.

cible. The negative pole placed in the cell consists of a very fine iron wire wound round a thicker one, and then covered with a piece of tobacco-pipe stem, so that only $\frac{1}{16}$th of an inch of it appears below; the positive pole is an iron cylinder, placed in the crucible round the cell. The heat should be regulated during the experiment, so that a crust may form in the cell; the metal will then collect under this crust without coming in contact with the sides of the crucible. In this manner, pieces of the metal weighing half a gramme are sometimes obtained.

Strontium resembles calcium in colour (p. 749), being only a shade darker; it oxidises much more quickly than that metal. Its specific gravity is 2·5418. Its place in the electrical series, with water as the exciting liquid, is as follows:

$$\overset{+}{K},\quad Na,\quad Li,\quad Ca,\quad Sr,\quad \overset{-}{Mg},\quad \&c.$$

Strontium burns like calcium, and acts similarly to it when heated in chlorine, oxygen, bromine, or iodine, or on boiling sulphur, or when thrown on water or acids. (Matthiessen.*)

Estimation of Strontium. — Strontium, like barium, may be estimated in the form of sulphate; but as sulphate of strontia is slightly soluble in water, it is necessary, in order to ensure complete precipitation, to add alcohol to the liquid, which may be done if there are no other substances present which are insoluble in alcohol.

Generally speaking, however, it is better to precipitate strontium in the form of a carbonate, by adding carbonate of ammonia and caustic ammonia, and heating the liquid. The precipitation of strontia in this form is more complete than that of baryta. The precipitate may be ignited on a lamp without giving off carbonic acid. It contains 59·27 per cent. of strontium, and 70·14 of strontia.

* Chem. Soc. Qu. J. viii. 107.

The same mode of precipitation serves to separate strontia from the alkalies.

The separation of strontia from baryta is best effected by means of hydrofluosilicic acid, which precipitates barium in the form of a crystalline silicofluoride, leaving the strontium in solution. The precipitate must be left to settle down for two or three hours; and its deposition may be accelerated by a gentle heat. It may then be collected on a weighed filter, washed with water, and dried at 100° C. The filtrate containing the strontium is then mixed with sulphuric acid, evaporated, and ignited, whereby it is converted into sulphate.

The quantities of barium and strontium in a mixture may likewise be determined by an indirect method, viz. by weighing them, first in the form of chlorides or carbonates, and afterwards as sulphates. Thus, suppose them to be first precipitated as carbonates, the united weight of which is found to be w, then converted into sulphates, the weight of which is w'. Then, to determine the quantity of baryta, x, and strontium, y, in the mixture, we have the equations

$$\frac{\dot{\mathrm{Ba}}\ddot{\mathrm{C}}}{\dot{\mathrm{Ba}}}x + \frac{\dot{\mathrm{Sr}}\ddot{\mathrm{C}}}{\dot{\mathrm{Sr}}}y = w; \quad \frac{\dot{\mathrm{Ba}}\dddot{\mathrm{S}}}{\dot{\mathrm{Ba}}}x + \frac{\dot{\mathrm{Sr}}\dddot{\mathrm{S}}}{\dot{\mathrm{Sr}}} = w';$$

$$\text{or,} \quad \frac{98{\cdot}7}{76{\cdot}7}x + \frac{73{\cdot}7}{51{\cdot}7}y = w; \quad \frac{116{\cdot}7}{76{\cdot}7}x + \frac{91{\cdot}7}{51{\cdot}7}y = w'.$$

A similar method may be applied in all cases in which two substances in a mixture can be weighed in two distinct forms. Such methods, however, give exact results only when the quantities of the substances to be determined are not very unequal.

CALCIUM.

Preparation. — A mixture of 2 at. chloride of calcium and 1 at. chloride of strontium, with a small quantity of chloride of ammonium (this mixture being more fusible than chloride of calcium alone), is melted in a small porcelain crucible, in which a carbon positive pole is placed, while a thin harpsichord wire wound round a thicker one, and dipping only just below the surface of the melted salt, forms the negative pole. The calcium is then reduced in beads, which hang on to the fine wire, and may be separated by withdrawing the negative pole every two or three minutes, together with the small crust which forms round it. A surer method, however of obtaining the metal, though in very small beads, is to place a pointed iron wire so as merely to touch the surface of the liquid ; the great heat evolved, owing to the resistance of the current, causes the reduced metal to fuse and drop off from the point of the wire, and the bead is taken out of the liquid with a small iron spatula. Or, thirdly, the disposition of the apparatus may be the same as that for the reduction of strontium (p. 746).

Properties.—Calcium is a light yellow metal, of the colour of gold alloyed with silver ; on a freshly cut surface, the lustre somewhat diminishes the yellow colour, which becomes more apparent when the light is reflected several times from two surfaces of calcium, or when the surface is slightly oxidised. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates having the thickness of the finest paper. Its specific gravity is 1·5778. In dry air the metal retains its colour and lustre for a few days, but in damp air the whole mass is slowly oxidised. Heated on platinum-foil over a spirit-lamp, it burns with a very bright flash. It is not quickly acted upon by dry chlorine at ordinary temperatures; but when heated, burns in that gas with

a most brilliant light; also in iodine, bromine, oxygen, sulphur, &c. With phosphorus, it combines without ignition, forming phosphide of calcium. Heated mercury dissolves it as a white amalgam. Calcium rapidly decomposes water, and is still more rapidly acted on by dilute nitric, hydrochloric, and sulphuric acids, nitric acid often causing ignition. Strong nitric acid does not act upon it below the boiling heat. In the voltaic circuit, with water as the liquid element, calcium is negative to potassium and sodium, but positive to magnesium. It is not, however reduced by potassium or sodium from its chloride by electrolysis. On the contrary, a fused mixture of CaCl with KCl or NaCl, in certain proportions, yields potassium or sodium, when subjected in a certain manner to electric action (p. 730); hence it appears that the metal formerly obtained by reducing chloride of calcium with potassium or sodium, could not be calcium, but was, probably, a mixture of potassium or sodium with aluminium, silicon, &c. (Matthiessen.*)

Lime. — According to Wittstein†, 1 part by weight of lime dissolves in 729 to 723 pts. of water, at ordinary temperatures, and in 1310 to 1569 pts. of boiling water. The carbonate of lime deposited from lime-water on exposure to the air is really the neutral carbonate, $CaO \cdot CO_2$.

Marchand and Scheerer find that *calcspar* begins to give off carbonic acid at 200° C., but that a certain quantity of that acid remains with the lime, even after the most violent ignition.‡

Sulphate of Lime dissolves in water containing sal-ammoniac more abundantly than in pure water, part of it appearing to be decomposed into chloride of calcium and sulphate of ammonia. The presence of nitrate of potash likewise increases the solubility of gypsum. (A. Vogel, jun.§)

* Chem. Soc. Qu. J. viii. 28.

† Repert. Pharm. [3], i. 182.

‡ J. pr. Chem. l. 237.

§ Repert. Pharm. [3], v. 342.

Sulphate of Lime and Potash, $KO.SO_3 + CaO.SO_3 + HO$. —This salt is obtained as an accessory product in the manufacture of tartaric acid from cream of tartar. The latter salt is converted, by treatment with carbonate of lime, into tartrate of lime and neutral tartrate of potash; and by the action of sulphate of lime, all the tartaric acid is obtained in combination with lime, together with an impure solution of sulphate of potash. This solution, when evaporated, yields a hard deposit, and in slowly evaporating large quantities of it, transparent laminated crystals are obtained, having the composition expressed by the above formula; they are sparingly soluble in water, more easily in dilute hydrochloric acid. The non-crystalline deposit contains about 65 per cent. of this double salt, together with sulphate, carbonate, and phosphate of lime, carbonate of magnesia, silicate of potash, oxide of iron, alumina, water, and traces of organic matter. (J. A. Phillips.*)

Phosphate of Lime.—According to H. Ludwig†, the precipitate produced by ordinary phosphate of soda in a solution of chloride of calcium mixed with ammonia, has, after washing and drying in the air, the composition $3CaO.PO_5 + 5\frac{1}{2}HO$; after keeping for two years in a loosely stoppered bottle, it is reduced to $3CaO.PO_5 + 3\frac{1}{2}HO$, and of these $3\frac{1}{2}HO$, $2\frac{1}{2}$ go off below 100°. The precipitate was free from chlorine, but contained a trace of ammonia.

According to Forchhammer‡, *apatite* may be artificially crystallised by fusing tribasic phosphate of lime, or bone-ash, with four times its weight of chloride of sodium, and leaving the fused mass to cool slowly. The mass when cold exhibits cavities containing numerous delicate six-sided prisms, having the composition of apatite.

Estimation of Calcium.—The metal may be estimated either as carbonate or as sulphate. The best method of precipitating

* Chem. Soc. Qu. J. iii. 348.

† Pharm. Centr. 1852, 345.

‡ Pogg. Ann. xci. 588.

it is, in most cases, by means of oxalate of ammonia, the oxalate being the least soluble of all the salts of calcium. If the solution contains an excess of any strong acid, such as nitric or hydrochloric acid, it must be neutralised with ammonia before adding the oxalate of ammonia, because oxalate of lime is soluble in the stronger acids. The precipitate, after being washed with hot water and dried, is heated over a lamp, care being taken not to allow the heat to rise above redress. It is thereby converted into carbonate of lime, containing 40·15 p. c. of calcium and 56·12 of lime.

If, however, the solution contains any acid which forms with lime a compound insoluble in water, phosphoric or boracic acid for example, this method of precipitation cannot be adopted; because, on neutralising with ammonia, the lime would be precipitated in combination with that acid, and would not be converted into oxalate on addition of oxalate of ammonia. In such a case, the lime may be precipitated as sulphate by adding pure dilute sulphuric acid and alcohol. The sulphate, when dried, contains 41·25 per cent. of lime. Phosphate of lime may, however, be precipitated from its acid solutions by oxalate of ammonia, with addition of acetate of ammonia, because oxalate of lime is insoluble in acetic acid, which dissolves the phosphate with facility.

From the *alkalies*, lime is easily separated either by oxalate of ammonia, or by sulphuric acid and alcohol.

Lime is separated from *baryta* by precipitating both the earths as carbonates, dissolving the carbonates in nitric acid, evaporating to dryness, and digesting the residue in absolute alcohol, which dissolves nitrate of lime, but not nitrate of baryta. They may also be separated in this manner in the form of chlorides, but the separation is less complete, because chloride of barium is not quite insoluble in absolute alcohol.

From *strontia*, lime is separated in the same manner, nitrate of strontia being likewise insoluble in alsolute alcohol.

When baryta, strontia, and lime occur together, the baryta

is first separated by hydro-fluosilicic acid; the strontia and lime in the filtrate are then converted into sulphates; these sulphates, after being weighed, converted into carbonates by fusion with carbonate of soda, or by boiling with the aqueous solution of that salt (p. 598); the carbonates weighed; and the quantities of strontia and lime determined from the equations:

$$\frac{91{\cdot}7}{51{\cdot}7}x + \frac{68}{28}y = w$$

$$\frac{73{\cdot}7}{51{\cdot}7}x + \frac{50}{28}y = w';$$

in which x is the weight of strontia, y that of the lime, w that of the sulphates, and w' that of the carbonates of the two bases. Or the carbonates may be dissolved in nitric acid, and the nitrates separated by absolute alcohol.

MAGNESIUM.

Bunsen prepares this metal by the electrolysis of the fused chloride. A porcelain crucible is divided in its upper part into two halves by a vertical diaphragm (made out of a thin porcelain crucible-cover), and fitted with a cover (filed from a tile), through which the extremities of the carbon-poles of a galvanic battery are introduced into the two halves of the crucible. The crucible is then heated to redness, together with the cover and the poles; filled with fused chloride of magnesium (I. 595); and subjected to the action of a battery of 10 zinc-carbon elements. The negative pole is cut like a saw, so that the magnesium, as it separates, may lodge in the cavities, and not float on the surface of the specifically heavier liquid.* According to Matthiessen †, the metal may be much more easily obtained from a fused mixture of 4 at. chloride of magnesium and 3 at. chloride of potassium, which is pre-

* Ann. Ch. Pharm. 82, 137.

† Chem. Soc. Qu. J. viii. 107.

pared with more facility than the pure anhydrous chloride of magnesium. The two salts mixed in the proper proportions* with a little chloride of ammonium may be fused and electrolysed in Bunsen's apparatus just described, the cutting of the negative pole being, however, dispensed with, as the metal is heavier than the fused mixture. A very simple and convenient way of reducing the metal, especially for the lecture-table, is to fuse the mixture in a common clay tobacco-pipe over an argand spirit-lamp or gas-burner, the negative pole being an iron wire passed up the pipe-stem, and the positive a piece of gas-coke, just touching the surface of the fused chlorides. (Matthiessen.)

Magnesium may, however, be obtained in much larger quantity, by heating a mixture of 600 grammes of chloride of magnesium, 100 grms. fused chloride of sodium, and 100 grms. of pulverised fluoride of calcium, with 100 grms. of sodium, to bright redness, in a covered earthen crucible. The magnesium is thereby obtained in globules, which are afterwards heated nearly to whiteness in a boat of compact charcoal placed within an inclined tube of the same material, through which a stream of dry hydrogen is passed. The magnesium then volatilises and condenses in the upper part of the tube. Lastly, it is remelted with a flux composed of chloride of magnesium, chloride of sodium, and fluoride of calcium, and is thus obtained in large globules. (H. Deville and Caron.†)

Magnesium on the recently fractured surface is sometimes slightly crystalline and coarsely laminated; sometimes fine-grained. In the former cases it is silver-white and shining; in the latter, bluish grey and dull. Its specific gravity is 1·7430 at + 5° C. (Bunsen); 1·75, according to Deville and Caron. It is about as hard as calcspar, and may be easily filed, bored, sawn, and flattened to a certain extent, but is scarcely more duc-

* The solution of the chloride of magnesium may be evaporated almost to dryness and analysed to find the proportion of anhydrous salt present.

† Ann. Ch. Pharm. ci. 359.

tile than zinc at ordinary temperatures. It melts at a moderate red heat (Bunsen); melts and volatilises at about the same temperature as zinc (Deville and Caron). It does not alter in a dry atmosphere, but in damp air soon becomes covered with a film of hydrate of magnesia. Heated to redness in the air, or in oxygen gas, it burns with a dazzling white light, and forms magnesia. It decomposes pure cold water but slowly, acidulated water very quickly; when thrown on aqueous hydrochloric acid, it takes fire momentarily; strong sulphuric acid dissolves it but slowly; a mixture of sulphuric acid and fuming nitric acid does not act upon it at ordinary temperatures. It burns when heated in chlorine gas; also in bromine-vapour, though with less facility; in sulphur and iodine-vapour very brilliantly (Bunsen).

Estimation of Magnesium. — When magnesia occurs in a solution not containing any other fixed substance, its quantity may be determined by evaporating to dryness, igniting the residue, then moistening it with sulphuric acid slightly diluted with water, and expelling the excess of that acid at a low red heat; sulphate of magnesia then remains, containing 33·7 per cent. of magnesia.

If the solution contains other fixed substances, the magnesia must be precipitated by the addition of ammonia in excess and phosphate of soda. The precipitated ammonio-magnesian phosphate is then treated in the manner described at p. 700. The pyrophosphate of magnesia obtained by igniting it contains 36 33 per cent. of magnesia.

From *baryta* and *strontia*, magnesia is separated by sulphuric acid; from lime, by oxalate of ammonia, with addition of chloride of ammonium to prevent the precipitation of the magnesia.

From the *alkalies*, magnesia may be separated by converting the bases into sulphates, and adding baryta-water. The magnesia is then precipitated in the form of hydrate, together with sulphate of baryta. The precipitate, after washing, is digested with dilute sulphuric acid, which extracts

the magnesia in the form of sulphate; and the filtrate containing the alkalies together with the excess of baryta, is also treated with sulphuric acid, which precipitates the baryta, and converts the alkalies into sulphates.

ALUMINIUM OR ALUMINUM.

Preparation. — This metal is now obtained in considerable quantity by decomposing the chloride or fluoride with sodium. The chloride of aluminium is prepared on the large scale by passing chlorine over a previously ignited mixture of clay and coal-tar in retorts like those used in the preparation of coal-gas, and is either made to pass into a chamber lined with plates of earthenware, where it condenses into a compact crystalline mass; or the vapour is made to pass over chloride of sodium at a red heat, whereby it is converted into the double chloride of aluminium and sodium. To effect the reduction, 400 pts. of this double salt, 200 pts. of chloride of sodium, 200 pts. of fluor-spar (or better, of cryolite), all perfectly dry and finely pounded, are mixed together, and the mixture placed, together with 75 or 80 parts of sodium, in an earthern crucible, the saline mixture and the sodium being deposited in alternate layers. The crucible is then moderately heated till the action begins, afterwards to redness, the melted mass stirred with an earthenware rod, and afterwards poured out. Twenty parts of aluminium are thus obtained in a compact lump, and about 5 parts in globules encrusted with a grey mass. (H. Ste-Claire Deville.*)

Aluminium may also be prepared in a similar manner from cryolite, the native fluoride of aluminium and sodium which is now imported in large quantities from Greenland. (H. Rose.†) Instead of this natural mineral, an artificial cry-

* Ann. Ch. Phys. [3], xlvi. 415; see also Compt. rend. xxxviii. 279; xl. 1298.

† Pogg. Ann. xcvi. 152.

olite may be used, prepared by mixing 1 part of burnt clay with 3 parts, or rather more, of anhydrous carbonate of soda, supersaturating the mixture with hydrofluoric acid, then drying and fusing it at a red heat. A fluoride of aluminium and potassium possessing analogous properties may be prepared by a similar process. (Deville.*)

Aluminium may likewise be obtained by the electrolysis of the double chloride of aluminium and sodium, the process being similar to that adopted by Bunsen for the electrolysis of chloride of magnesium. (Deville, Bunsen.)

Pure aluminium is a white metal, with a faint bluish iridescence; when recently fused, it is soft like pure silver, and has a density of 2·56; but after hammering or rolling, it is as hard as iron, and has a density of 2·67. A bar of it is very sonorous. It conducts electricity eight times as well as iron, and is slightly magnetic. Its melting point is between those of zinc and silver: when solidified from fusion, or reduced by electrolysis, it exhibits crystalline forms, apparently regular octohedrons. It does not oxidise in the air, even at a strong red heat; neither does it decompose water, excepting at the strongest red heat,—and even then but slowly. It does not dissolve in nitric acid, either dilute or concentrated, at ordinary temperatures, and but very slowly in boiling nitric acid; dilute sulphuric acid scarcely attacks it at ordinary temperatures, even after a long time; but hydrochloric acid, at any degree of concentration, dissolves it readily, even at low temperatures, with evolution of hydrogen. It is not attacked by hydrosulphuric acid, or by the fused hydrates of the alkalies. It does not combine with mercury, and when fused with lead, takes up only traces of that metal. With copper it unites in various proportions, forming light, very hard, white alloys, and it combines also with silver and iron. (Deville.)

* Ann. Ch. Phys. [3], xlix. 83.

Alumina. — The specific gravity of alumina ignited over a spirit-lamp is from 3·87 to 3·90; after 6 hours' ignition in an air-furnace, 3·75 to 3·725; and after ignition in a porcelain furnace, 3·999, which agrees very nearly with that of naturally crystallised alumina as it occurs in the ruby, sapphire, and corundum. (H. Rose.*)

Bihydrate of Alumina, soluble in water, $Al_2O_3 + 2HO$. When a dilute solution of biacetate of alumina (see page 760), is exposed to heat for several days, the whole of the acetic acid appears to become free, and the alumina passes into an allotropic state in which it is *soluble in water,* and is no longer capable of acting as a mordant, or of entering into any definite combination. This allotropic alumina retains 2 at. water when dried at 100° C. Its solution is coagulated by mineral acids and by most vegetable acids, by alkalies, by a great number of neutral salts, and by decoctions of dye-woods. It is insoluble in the stronger acids, but soluble in acetic acid, unless it has been previously coagulated in the manner just mentioned. Boiling potash changes it into the ordinary terhydrate. Its coagulum with dye-woods has the colour of the infusion, but is translucent, and entirely different from the dense opaque cakes which ordinary alumina forms with the same colouring matters. (Walter Crum.†)

According to Phillips ‡, hydrate of alumina when kept after precipitation in a moist atmosphere or under water, becomes after a few days difficult to dissolve in acids.

Alum. — By fusing ignited alumina with four times its weight of bisulphate of potash, a mass is obtained, which when treated with warm water, leaves an insoluble residue, consisting of thin microscopic six-sided tables, which refract light singly. They contain 23 per cent. potash, 30·7 sulphuric acid, and 46·3 alumina, and appear to consist of crystallised anhydrous alum. (Salm-Horstmar.§)

* Pogg. Ann. lxxiv. 430.
† Chem. Soc. Qu. J. vii. 225.
‡ Chem. Gaz. 1848, 349.
§ J. pr. Chem. lii. 319.
‖ Sill. Am. J. [2], ix. 30.

Nitrate of Alumina.— According to Ordway‖, a concentrated and somewhat acid solution of alumina in nitric acid, deposits colourless, flattened, oblique rhombic prisms, containing $Al_2O_3 . 3NO_5 + 18HO$. These crystals melt at 72·8° C. into a colourless liquid which solidifies in the crystalline form on cooling; they are deliquescent, and dissolve in water and in nitric acid. Half an ounce of the pulverised crystals mixed with an equal weight of bicarbonate of ammonia, lowered the temperature from 10·5° to −23·3° C. By the action of this salt upon hydrate of alumina, basic salts appear to be formed. Salm-Horstmar*, by evaporating and cooling a solution of hydrate of alumina in nitric acid of 26·3 per cent. likewise obtained a salt which crystallised in rhombic prisms and (by truncation) in hexagonal tables; but after repeated solution in water, it no longer crystallised distinctly; and its aqueous solution was decomposed by evaporation at a somewhat elevated temperature.

Acetates of Alumina.—By decomposing tersulphate of alumina (I., p. 605), with neutral acetate of lead, a solution is formed, consisting apparently of a mixture of biacetate of alumina with 1 at. free acetic acid.

When this aluminous solution is evaporated at a low temperature and with sufficient rapidity,—as by spreading the concentrated solution very thinly over sheets of glass or porcelain, exposing it to a temperature not exceeding 100° F., and, as it runs together in drops, rubbing it constantly with a platinum or silver spatula,—a dry substance is obtained which may be redissolved easily and entirely by water. This is the biacetate of alumina, $Al_2O_3 . 2C_4H_3O_3 + 4HO$: the alumina contained in it retains all its usual properties.

When the first aluminous solution, containing not less than 4 or 5 per cent. of alumina, is left for some days in the cold, a salt is deposited in the form of a white crust, which is an *allotropic biacetate of alumina insoluble in water.* Heat effects

* J. pr. Chem. lix. 208.

the same change in the aluminous solution more rapidly, and the insoluble biacetate then separates in the form of a granular powder. At the boiling temperature, the liquid is thus deprived, in half an hour, of the whole of its alumina, which goes down with $\frac{2}{3}$ of the acetic acid, leaving $\frac{1}{3}$ in the liquid.

The soluble biacetate of alumina is decomposed by heat, yielding the bihydrate of alumina soluble in water already described (p. 758). The insoluble biacetate of alumina, when digested in a large quantity of water, is gradually changed into the soluble biacetate, part of which, however, is decomposed during the process into acetic acid and the allotropic bihydrate of alumina.

The precipitate which is formed on the application of heat to a mixed solution of acetate of alumina and sulphate of potash, and which is soluble in cold acetic acid, is a bibasic sulphate of alumina, $2Al_2O_3 \cdot SO_3 + 10HO$.

Common salt added to a solution of teracetate of alumina forms, on the application of heat, a very finely divided white precipitate containing 44·66 per cent. alumina, 21·96 acetic acid, 5·51 hydrochloric acid, 25·90 water, and 1·97 chloride of sodium. A similar precipitate is formed by nitrate of potash (Walter Crum.*)

Estimation of Alumina.—Alumina is precipitated from its solutions in the form of hydrate by ammonia, carbonate of ammonia, or sulphide of ammonium; the precipitate when ignited yields pure anhydrous alumina, containing 53·26 per cent. of the metal.

Precipitation with ammonia or sulphide of ammonium serves also to separate alumina from the preceding bases. In thus separating it from the alkaline earths, care must be taken not to expose the liquid to the air; otherwise carbonic acid will be absorbed by the excess of ammonia, and the alkaline earths precipitated as carbonates. From baryta, alumina is most readily separated by sulphuric acid.

* Chem. Soc. Qu. J. vii. 217.

GLUCINUM.

This metal and its compounds have been minutely examined by Debray.* The metal may be obtained from the chloride by reduction with sodium. It is a white metal, whose density is 2·1. It may be forged, and rolled into sheets like gold. Its melting-point is below that of silver. It may be melted in the outer blowpipe-flame, without exhibiting the phenomenon of ignition presented by zinc and iron under the same circumstances; it cannot even be set on fire in an atmosphere of pure oxygen, but in both experiments becomes covered with a thin coat of oxide, which seems to protect it from further change. It does not appear to combine with sulphur under any circumstances, but unites directly with chlorine and iodine with the aid of heat. Silicon unites readily with glucinum, forming a hard brittle substance susceptible of a high polish; this alloy is always formed when glucinum is reduced in porcelain vessels. Glucinum does not decompose water at a boiling heat, or even when heated to whiteness. Sulphuric and hydrochloric acid dissolve it, with evolution of hydrogen. Nitric acid, even when concentrated, does not act upon it at ordinary temperatures, and dissolves it but slowly at a boiling heat. Glucinum is not attacked by ammonia, but dissolves readily in caustic potash.

The above-mentioned properties differ considerably from those of the metal which Wöhler obtained by igniting chloride of glucinum with potassium in a platinum crucible; the metal thus obtained being a grey powder, very refractory in the fire, but combining with oxygen, sulphur, and chlorine much more energetically than Debray's metal. The differences appear to be due, partly to the different states of aggregation, and partly to the contamination of Wöhler's metal with platinum and potassium.

* Ann. Ch. Phys. [3], xliv. 5.

Glucina.—Debray prepares this earth from the emerald of Limoges by the following process. The mineral, finely pounded (levigation with water is quite superfluous), is fused with half its weight of quicklime in an air-furnace, and the glass thus obtained is treated, first with dilute, and then with strong nitric acid, till it is reduced to a homogeneous jelly. The product is then evaporated to dryness, and heated sufficiently to decompose the nitrates of alumina, glucina, and iron, and a small portion of the nitrate of lime; and the residue, consisting of silica, alumina, glucina, sesquioxide of iron, nitrate of lime, and a small quantity of free lime, is boiled with water containing sal-ammoniac, which dissolves the nitrate of lime immediately, and the free lime after a while, with evolution of ammonia. (If no ammonia is evolved, the calcination has not been carried far enough and must be repeated.) The liquid is then decanted; the precipitate, after thorough washing, treated with boiling nitric acid; and the resulting solution of alumina, glucina, and iron poured into a solution of carbonate of ammonia mixed with free ammonia. The earths are thereby precipitated without evolution of carbonic acid, and the glucina redissolves, after seven or eight days, in the excess of carbonate of ammonia. As the carbonate of ammonia may also dissolve a small quantity of iron, it should be mixed with a little sulphide of ammonium to precipitate the iron completely. Lastly, the carbonate of ammonia is distilled off, and the carbonate of glucina which remains yields pure glucina by calcination.

Glucina is not hardened by heat like alumina, but merely rendered less soluble in acids. Ebelmen has obtained it in hexagonal prisms by exposing a solution of glucina in fused boracic acid to a powerful and long-continued heat. It may be more easily obtained in microscopic crystals, apparently of the same form, by decomposing the sulphate at a high temperature in presence of sulphate of potash, also by calcining the double carbonate of glucina and ammonia.

Hydrate of glucina dissolves in potash like alumina, but is reprecipitated by boiling when the solution is diluted with water to a certain extent. It is likewise soluble in carbonate of potash or soda, sulphurous acid, and bisulphite of ammonia. When precipitated by ammonia, especially from the oxalate or acetate, it is completely redissolved by prolonged ebullition.

Glucina was regarded by Berzelius as a sesquioxide, Gl_2O_3, while Awdejew and others regard it as a protoxide, GlO. The latter formula appears preferable, first because it gives more simple formulæ for the salts of glucina than the former, and secondly, because glucina, on the whole, exhibits a closer resemblance to known protoxides, such as magnesia, than to sesquioxides, such as alumina. The greater simplicity of the formulæ derived from the formula GlO, will be seen from the following table:

Neutral sulphate of glucina . .	$GlO.SO_3 + 4HO$ or $Gl_2O_3.SO_3 + 12HO$.
Sulphate of glucina and potash .	$KO.SO_3 + GlO.SO_3 + 3HO$ or $3(KO.SO_3) + Gl_2O_3.3SO_3 + 6HO$.
Carbonate of glucina and ammonia	$3(NH_4O.CO_2) + 4GlO.3CO_2 + HO$ or $9(NH_4O.CO_2) + 4Gl_2O_3.9CO_2 + 3HO$.
Oxalate of glucina and potash .	$KO.C_2O_3 + GlO_2C_2O_3$ or $3(KO.C_2O_3) + Gl_2O_3.3C_2O_3$.

The reasons which induced Berzelius to regard glucina as a sesquioxide, were founded on the resemblance of glucina and alumina in the hydrated state, from the volatility of the chlorides, and from the supposed capability of glucina and alumina to replace one another in minerals, as in cymophane and in emerald. This last point has been completely settled by the researches of Awdejew and of Damour, from which it appears that cymophane, the native aluminate of glucina, has always the same composition ($GlO.Al_2O_3$), from whatever locality it may be derived. With regard to the hydrates, it is true that alumina and glucina are precipitated under the same circumstances; but there the resemblance ends. Glucina, when dried in the air, absorbs carbonic acid and forms a

carbonate, which alumina does not. The existence of a definitely crystallised carbonate of ammonia and glucina (obtained by boiling a solution of glucina in carbonate of ammonia, stopping the ebullition as soon as turbidity appears, then filtering, and adding alcohol) constitutes another important difference between that earth and alumina. The anhydrous oxides likewise differ essentially. Glucina volatilises, like magnesia, without melting, whereas alumina fuses under the same circumstances. Glucina cannot be fused with lime, like alumina, the presence of another body, such as silica or alumina, being required to enable the fusion to take place. In this respect again glucina resembles magnesia. The identity of crystalline form which has been observed between glucina and alumina is merely an isolated fact, which would be important if the two bodies possessed similar chemical properties, but not otherwise.

Chloride of glucinum exhibits at first sight considerable resemblance to chloride of aluminium, and is prepared in a similar manner; but the resemblance does not go far. Chloride of glucinum is less volatile than chloride of aluminium: thus, when a mixture of finely powdered emerald and charcoal, made into a paste with oil, is calcined in a crucible, then powdered, and heated in a porcelain tube through which chlorine gas is passed, chloride of glucinum and chloride of aluminium are formed together; but the chloride of glucinum passes over first, and may be separately condensed. Chloride of glucinum is, in fact, about as volatile as chloride of zinc. Chloride of aluminium unites with the alkaline chlorides, forming compounds which may be called *spinelles*, and are represented by the general formula $MCl + Al_2Cl_3$; but chloride of glucinum does not form any similar compound.

It must, however, be remembered that glucina does not exhibit any very close analogy to the class of protoxides. It is not isomorphous with lime or magnesia. Cymophane may be represented by the general formula of the spinelles,

$GlO . Al_2O_3$; but the dissimilarity of its crystalline form prevents it from being included in that class of minerals. The emerald also differs completely in crystalline form from the generality of silicates of the same composition, whose general formula is $MO . SiO_3 + M_2'O_3 . 3SiO_3$. Neither is there any greater analogy between the double sulphates, carbonates, and oxalates of glucina and those of lime or magnesia. On the whole, glucina appears to be intermediate in its properties between the protoxides and sesquioxides.

Glucina is precipitated from its solutions for quantitative analysis in the same manner as alumina. From the latter it is separated by carbonate of ammonia.

Note to Page 675.

Chloride of Silicon and Hydrogen, $Si_2Cl_8 . 2HCl$.— This is the compound which Wöhler and Buff obtained by heating crystalline silicon in a current of dry hydrochloric acid gas. It is a colourless, very mobile liquid, of sp. gr. 1·65, and boiling at 42° C. It has a very pungent odour, and fumes strongly in the air. Its vapour is as inflammable as ether-vapour, and burns with a faint greenish flame, diffusing vapours of silica and hydrochloric acid. When passed through a red-hot tube, it is decomposed, yielding hydrochloric acid, terchloride of silicon, and a specular deposit of amorphous silicon. The compound is decomposed by water with formation of a corresponding oxide.

The compounds $Si_2Br_3 . 2HBr$, and $Si_2I_3 . 2HI$, are obtained in a similar manner. The former is liquid, the latter solid, at ordinary temperatures.

Hydrated Oxide of Silicon.— $Si_2O_3 . 2HO$, is formed by

the action of water on either of the preceding compounds, but most easily from the chloride. It is a snow-white amorphous, very bulky powder, which floats on water. It is insoluble in all acids except hydrofluoric acid. Alkalies, even ammonia, dissolve it readily, with evolution of hydrogen and formation of an alkaline silicate.

It may be heated to 300° C. without alteration; but at higher temperatures, it glows brightly, and gives off spontaneously inflammable hydrogen gas (containing siliciuretted hydrogen).

A lower oxide of silicon (SiO?) and the corresponding chloride appear also to exist.*

* Ann. Ch. Pharm., Oct. 1857, p. 94.

TABLE A.

FOR CONVERTING FRENCH DECIMAL MEASURES AND WEIGHTS INTO ENGLISH MEASURES AND WEIGHTS.

1 Meter	=	1·0936331	English	yards.
	=	3·2808992	„	feet.
	=	39·37079	„	inches.
1 Liter	=	0·2209687	Imperial	gallons.
	=	1·7677496	„	pints.
	=	0·35317	cubic	feet.
	=	61·02710	„	inches.
1 Kilogramme	=	0·0196969	cwt.	
	=	2·20606	lb. (avoird.)	
	=	2·68098	lb. (troy).	
1 Gramme	=	15·44242	grains.	

These values are taken from the "Table of Constants" at the end of the Tables of Logarithms published by the Society for the Diffusion of Usefui Knowledge.

The Imperial Gallon is equal to 277·24 cubic inches, and contains 10 lbs. avoirdupois of water at 60° Fahr.

TABLE B.

BAROMETER SCALE IN MILLIMETERS AND INCHES.

Mm.		In.	Mm.		In.	Mm.		In.
700	=	27·560	730	=	28·741	760	=	29·922
701	=	27·599	731	=	28 780	761	=	29·962
702	=	27·639	732	=	28·820	762	=	30·001
703	=	27·678	733	=	28·859	763	=	30·040
704	=	27·717	734	=	28·899	764	=	30·080
705	=	27·756	735	=	28·938	765	=	30·119
706	=	27·795	736	=	28·977	766	=	30·159
707	=	27·835	737	=	29·017	767	=	30·198
708	=	27·875	738	=	29·056	768	=	30·237
709	=	27 914	739	=	29·096	769	=	30 277
710	=	27·954	740	=	29·135	770	=	30·316
711	=	27·993	741	=	29·174	771	=	30·355
712	=	28·032	742	=	29·214	772	=	30·395
713	=	28·072	743	=	29·253	773	=	30·434
714	=	28·111	744	=	29·292	774	=	30·474
715	=	28·151	745	=	29·332	775	=	30·513
716	=	28·190	746	=	29·371	776	=	30·552
717	=	28·229	747	=	29·411	777	=	30·592
718	=	28·269	748	=	29·450	778	=	30·631
719	=	28·308	749	=	29·489	779	=	30·671
720	=	28·347	750	=	29·529	780	=	30·710
721	=	28·387	751	=	29·568	781	=	30·749
722	=	28·426	752	=	29·607	782	=	30·788
723	=	28·466	753	=	29·647	783	=	30·828
724	=	28·505	754	=	29·686	784	=	30·867
725	=	28·544	755	=	29·725	785	=	30·907
726	=	28·584	756	=	29·765	786	=	30·946
727	=	28 623	757	=	29·804	787	=	30·985
728	=	28 662	758	=	29·844	788	=	31·025
729	=	28·702	759	=	29·882	789	=	31·064

28 inches = 711·187 millimeters.
29 „ = 736·587 „
30 „ = 761·986 „
31 „ = 787·386 „

1 millimeter = 0·03937079 inch. | 1 inch = 25·39954 millimeters.

TABLE C.

FOR CONVERTING DEGREES OF THE CENTIGRADE THERMOMETER INTO DEGREES OF FAHRENHEIT'S SCALE.

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
− 100°	− 148·0°	− 50°	− 58·0°	0°	+ 32·0°
99	146·2	49	56·2	+ 1	33·8
98	144·4	48	54·4	2	35·6
97	142·6	47	52·6	3	37·4
96	140·8	46	50·8	4	39·2
95	139·0	45	49·0	5	41·0
94	137·2	44	47·2	6	42·8
93	135·4	43	45·4	7	44·6
92	133·6	42	43·6	8	46·4
91	131·8	41	41·8	9	48·2
90	130·0	40	40·0	10	50·0
89	128·2	39	38·2	11	51·8
88	126·4	38	36·4	12	53·6
87	124·6	37	34·6	13	55·4
86	122·8	36	32·8	14	57·2
85	121·0	35	31·0	15	59·0
84	119·2	34	29·2	16	60·8
83	117·4	33	27·4	17	62·6
82	115·6	32	25·6	18	64·4
81	113·8	31	23·8	19	66·2
80	112·0	30	22·0	20	68·0
79	110·2	29	20·2	21	69·8
78	108·4	28	18·4	22	71·6
77	106·6	27	16·6	23	73·4
76	104·8	26	14·8	24	75·2
75	103·0	25	13·0	25	77·0
74	101·2	24	11·2	26	78·8
73	99·4	23	9·4	27	80·6
72	97·6	22	7·6	28	82·4
71	95·8	21	5·8	29	84·2
70	94·0	20	4·0	30	86·0
69	92·2	19	2·2	31	87·8
68	90·4	18	0·4	32	89·6
67	88·6	17	+ 1·4	33	91·4
66	86·8	16	3·2	34	93·2
65	85·0	15	5·0	35	95·0
64	83·2	14	6·8	36	96·8
63	81·4	13	8·6	37	98·6
62	79·6	12	10·4	38	100·4
61	77·8	11	12·2	39	102·2
60	76·0	10	14·0	40	104·0
59	74·2	9	15·8	41	105·8
58	72·4	8	17·6	42	107·6
57	70·6	7	19·4	43	109·4
56	68·8	6	21·2	44	111·2
55	67·0	5	23·0	45	113·0
54	65·2	4	24·8	46	114·8
53	63·4	3	26·6	47	116·6
52	61·6	2	28·4	48	118·4
51	59·8	1	30·2	49	120·2

TABLE C.—(*continued.*)

Cent.		Fah.	Cent		Fah.	Cent.		Fah.
+ 50°	...	+ 122·0°	+ 100°	...	+ 212·0°	+ 150°	...	+ 302·0°
51	...	123·8	101	...	213·8	151	...	303·8
52	...	125·6	102	...	215·6	152	...	305·6
53	...	127·4	103	...	217·4	153	...	307·4
54	...	129·2	104	...	219·2	154	...	309·2
55	...	131·0	105	...	221 0	155	...	311·0
56	...	132·8	106	...	222·8	156	...	312·8
57	...	134·6	107	...	224·6	157	...	314·6
58	...	136·4	108	...	226·4	158	...	316·4
59	...	138·2	109	...	228·2	159	...	318·2
60	...	140·0	110	...	230·0	160	...	320·0
61	...	141·8	111	...	231·8	161	...	321·8
62	...	143·6	112	...	233·6	162	...	323·6
63	...	145·4	113	...	235·4	163	...	325·4
64	...	147·2	114	...	237·2	164	...	327·2
65	...	149·0	115	...	239·0	165	...	329 0
66	...	150·8	116	...	240·8	166	...	330·8
67	...	152·6	117	...	242·6	167	...	332·6
68	...	154·4	118	...	244·4	168	...	334·4
69	...	156·2	119	...	246·2	169	...	336·2
70	...	158·0	120	...	248·0	170	...	338·0
71	...	159·8	121	...	249·8	171	...	339·8
72	...	161·6	122	...	251·6	172	...	341·6
73	...	163·4	123	...	253·4	173	...	343·4
74	...	165·2	124	...	255·2	174	...	345·2
75	...	167·0	125	...	257·0	175	...	347·0
76	...	168·8	126	...	258·8	176	...	348·8
77	...	170·6	127	...	260·6	177	...	350·6
78	...	172·4	128	...	262·4	178	...	352·4
79	...	174·2	129	...	264·2	179	...	354·2
80	...	176·0	130	...	266·0	180	...	356·0
81	...	177·8	131	...	267·8	181	...	357·8
82	...	179·6	132	...	269·6	182	...	359·6
83	...	181·4	133	...	271·4	183	...	361·4
84	...	183·2	134	...	273·2	184	...	363·2
85	...	185·0	135	...	275·0	185	...	365·0
86	...	186·8	136	...	276·8	186	...	366·8
87	...	188·6	137	...	278·6	187	...	368·6
88	...	190·4	138	...	280·4	188	...	370·4
89	...	192·2	139	...	282·2	189	...	372·2
90	...	194·0	140	...	284·0	190	...	374·0
91	...	195·8	141	...	285·8	191	...	375·8
92	...	197·6	142	...	287·6	192	...	377·6
93	...	199·4	143	...	289·4	193	...	379·4
94	...	201·2	144	...	291·2	194	...	381·2
95	...	203·0	145	...	293·0	195	...	383·0
96	...	204·8	146	...	294·8	196	...	384·8
97	...	206·6	147	...	296·6	197	...	386·6
98	...	208·4	148	...	298·4	198	...	388·4
99	...	210·2	149	...	300·2	199	...	390·2

TABLE C.—(*continued.*)

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
+ 200° ...	+ 392·0°	+ 250° ...	+ 482·0°	+ 300° ...	+ 572·0°
201 ...	393·8	251 ...	483·8	301 ...	573·8
202 ...	395 6	252 ...	485·6	302 ...	575·6
203 ...	397·4	253 ...	487·4	303 ...	577·4
204 ...	399·2	254 ...	489·2	304 ...	579·2
205 ...	401·0	255 ...	491·0	305 ...	581·0
206 ...	402·8	256 ...	492·8	306 ...	582·8
207 ...	404·6	257 ...	494·6	307 ...	584·6
208 ...	406·4	258 ...	496·4	308 ...	586·4
209 ...	408·2	259 ...	498·2	309 ...	588·2
210 ...	410·0	260 ...	500·0	310 ...	590·0
211 ...	411·8	261 ...	501·8	311 ...	591·8
212 ...	413·6	262 ...	503·6	312 ...	593·6
213 ...	415·4	263 ...	505·4	313 ...	595·4
214 ...	417·2	264 ...	507 2	314 ...	597·2
215 ...	419·0	265 ...	509·0	315 ...	599·0
216 ...	420·8	266 ...	510·8	316 ...	600·8
217 ...	422·6	267 ...	512·6	317 ...	602·6
218 ...	424·4	268 ...	514·4	318 ...	604·4
219 ...	426·2	269 ...	516·2	319 ...	606·2
220 ...	428·0	270 ...	518·0	320 ...	608·0
221 ...	429 8	271 ...	519·8	321 ...	609·8
222 ...	431·6	272 ...	521·6	322 ...	611·6
223 ...	433·4	273 ...	523·4	323 ...	613·4
224 ...	435·2	274 ...	525·2	324 ...	615·2
225 ...	437·0	275 ...	527·0	325 ...	617 0
226 ...	438 8	276 ...	528·8	326 ...	618·8
227 ...	440·6	277 ...	530·6	327 ...	620·6
228 ...	442·4	278 ...	532·4	328 ...	622·4
229 ...	444·2	279 ...	534·2	329 ...	624·2
230 ...	446·0	280 ...	536·0	330 ...	626·0
231 ...	447·8	281 ...	537·8	331 ...	627·8
232 ...	449·6	282 ...	539·6	332 ...	629 6
233 ...	451·4	283 ...	541·4	333 ...	631·4
234 ...	453·2	284 ...	543·2	334 ...	633·2
235 ...	455·0	285 ...	545·0	335 ...	635·0
236 ...	456·8	286 ...	546·8	336 ...	636·8
237 ...	458 6	287 ...	548·6	337 ...	638·6
238 ...	460·4	288 ...	550·4	338 ...	640·4
239 ...	462·2	289 ...	552·2	339 ...	642·2
240 ...	464·0	290 ...	554·0	340 ...	644·0
241 ...	465·8	291 ...	555·8	341 ...	645·8
242 ...	467·6	292 ...	557·6	342 ...	647·6
243 ...	469·4	293 ...	559·4	343 ...	649·4
244 ...	471·2	294 ...	561·2	344 ...	651·2
245 ...	473·0	295 ...	563·0	345 ...	663·0
246 ...	474·8	296 ...	564·8	346 ...	654·8
247 ...	476·6	297 ...	566·6	347 ...	656·6
248 ...	478·4	298 ...	568·4	348 ...	658·4
249 ...	480·2	299 ...	570·2	349 ...	660·2

TABLE D.

COMPARISON OF THE DEGREES OF BAUMÉ'S HYDROMETER WITH THE REAL SPECIFIC GRAVITIES.

1. *For Liquids heavier than Water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	26	1·206	52	1·520
1	1·007	27	1·216	53	1·535
2	1·013	28	1·225	54	1·551
3	1·020	29	1·235	55	1·567
4	1·027	30	1·245	56	1·583
5	1·034	31	1·256	57	1·600
6	1·041	32	1·267	58	1·617
7	1·048	33	1·277	59	1·634
8	1·056	34	1·288	60	1·652
9	1·063	35	1·299	61	1·670
10	1·070	36	1·310	62	1·689
11	1·078	37	1·321	63	1·708
12	1·085	38	1·333	64	1·727
13	1·094	39	1·345	65	1·747
14	1·101	40	1·357	66	1·767
15	1·109	41	1·369	67	1·788
16	1·118	42	1·381	68	1·809
17	1·126	43	1·395	69	1·831
18	1·134	44	1·407	70	1·854
19	1·143	45	1·420	71	1·877
20	1·152	46	1·434	72	1·900
21	1·160	47	1·448	73	1·924
22	1·169	48	1·462	74	1 949
23	1·178	49	1·476	75	1·974
24	1·188	50	1·490	76	2·000
25	1·197	51	1·495		

TABLE D. — (*continued*).

2. *Baumé's Hydrometer for Liquids lighter than Water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	27	0·896	44	0·811
11	0·993	28	0·890	45	0·807
12	0·986	29	0·885	46	0·802
13	0·980	30	0·880	47	0·798
14	0·973	31	0·874	48	0·794
15	0·967	32	0·869	49	0·789
16	0·960	33	0·864	50	0·785
17	0·954	34	0·859	51	0·781
18	0·948	35	0·854	52	0·777
19	0·942	36	0·849	53	0·773
20	0·936	37	0·844	54	0·768
21	0·930	38	0·839	55	0·764
22	0·924	39	0·834	56	0·760
23	0·918	40	0·830	57	0·757
24	0·913	41	0·825	58	0·753
25	0·907	42	0·820	59	0·749
26	0·901	43	0·816	60	0·745

Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water.

In the United Kingdom, Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real specific gravity can be deduced by an extremely simple method from the degree of the hydrometer, namely, by multiplying the latter by 5, and adding 1000 ; the sum is the specific gravity, water being 1000. Thus 10° Twaddell indicates a specific gravity of 1050, or 1·05 ; 90° Twaddell, 1450, or 1·45.

TABLE E.

SHOWING THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL IN 100 PARTS OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES. (FOWNES.)

Sp. Gr. at 60° F.	Percentage of real Alcohol.	Sp. Gr. at 60° F.	Percentage of real Alcohol.	Sp. Gr. at 60° F.	Percentage of real Alcohol.
·9991	0·5	·9511	34	·8769	68
·9981	1	·9490	35	·8745	69
·9965	2	·9470	36	·8721	70
·9947	3	·9452	37	·8696	71
·9930	4	·9434	38	·8672	72
·9914	5	·9416	39	·8649	73
·9898	6	·9396	40	·8625	74
·9884	7	·9376	41	·8603	75
·9869	8	·9356	42	·8581	76
·9855	9	·9335	43	·8557	77
·9841	10	·9314	44	·8533	78
·9828	11	·9292	45	·8508	79
·9815	12	·9270	46	·8483	80
·9802	13	·9249	47	·8459	81
·9789	14	·9228	48	·8434	82
·9778	15	·9206	49	·8408	83
·9766	16	·9184	50	·8382	84
·9753	17	·9160	51	·8357	85
·9741	18	·9135	52	·8331	86
·9728	19	·9113	53	·8305	87
·9716	20	·9090	54	·8279	88
·9704	21	·9069	55	·8254	89
·9691	22	·9047	56	·8228	90
·9678	23	·9025	57	·8199	91
·9665	24	·9001	58	·8172	92
·9652	25	·8979	59	·8145	93
·9638	26	·8956	60	·8118	94
·9623	27	·8932	61	·8089	95
·9609	28	·8908	62	·8061	96
·9593	29	·8886	63	·8031	97
·9578	30	·8863	64	·8001	98
·9560	31	·8840	65	·7969	99
·9544	32	·8816	66	·7938	100
·9528	33	·8793	67		

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ERRATA IN VOL. II.

Page	Line				
92	5 from top	for	Cor dHg_2	read	$CdHg_2$.
110	9 from bottom	,,	cadium	,,	cadmium.
142	11 ,,	,,	sulphide	,,	sulphides.
143	17 from top	,,	Odlings	,,	Odling
539	15 ,,	,,	$\left.\begin{matrix}P_2H_2\Theta_5\\H_2\end{matrix}\right\}\Theta_7$	,,	$\left.\begin{matrix}P_2H_2\Theta_5\\H_2\end{matrix}\right\}\Theta_2$
541	4 ,,	,,	$AsH_3\Theta_5$	,,	$AsH_3\Theta_4$.

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